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SOLIDS AND VAPORS.

By Wilder D. Bancroft.[1]

When a substance, having no appreciable vapor-pressure of its own, is dissolved in a liquid, the vapor-pressure of the solution is less than that of the pure solvent. From this it follows that if two beakers, one containing a salt solution and the other pure water, be placed under a bell-jar, the water will all distill over into the beaker containing the solution,[2] provided that we leave out of account any effect due to gravity. A further conclusion is that all substances are deliquescent in presence of the saturated vapor of a liquid in which they are soluble. As a striking example of this I have taken the blue double salt, $CuCl_2\ 2\ KCl\ 2\ H_2O$. This salt was placed in a test-tube above absolute alcohol, so that any liquid that condensed upon it might flow back into the bottom of the test-tube again. The result was that the cupric chloride was dissolved out, leaving the white potassium chloride behind.

As the vapor-pressures of pure water and of a saturated salt solution are functions of the temperature only, it follows that, if the other conditions are kept constant, water must condense on the salt solution at an uniform rate so long as any of the solid salt is

[1] In my paper on the Chemical Potential of the Metals, Physical Review, Vol. III., p. 253, 1896, I overlooked very carelessly the definite assumption of Nernst, Zeitschr. f. phys. Chem., 4, p. 149, 1889, in regard to the anion.

[2] Cf. Beyerinck, Zeitschr. f. phys. Chem., 9, p. 264, 1892.

present. I tried the experiment at first very roughly by putting a little ammonium chloride in a small porcelain crucible, which was then placed in a desiccator containing water instead of sulfuric acid. The whole was left at room temperature; the crucible was weighed from time to time, and the gain in weight noted. While there could be no doubt but that the ammonium chloride would absorb water, I was not at all sure that the amount absorbed in a given time would be enough to make the experiment of any value. In this I was agreeably surprised, as I found that under these circumstances the salt gained water at the rate of about twelve milligrams per hour. The rate of absorption is dependent on the difference of pressure between the solvent and the solution, on the areas of the evaporating and condensing surfaces, and on the rate of diffusion of water-vapor under the conditions of the experiment. Whether there is also an effect due to the specific nature of the dissolved substance apart from the vapor-pressure of its saturated solution is not known. Such an effect would be entirely contrary to our present ways of looking at things; but that does not prove its non-existence. With so many factors to be taken into account, it is very difficult to make absolute measurements. On the other hand, it is a comparatively simple matter to make relative determinations which are entirely satisfactory for a great many purposes. The uncertainty as to the amount of surface of the solid salt can be obviated by having a saturated solution in a cylindrical vessel so that the condensation takes place on a liquid surface only. By setting up the apparatus always in the same way, it would not be necessary, so far as purposes of direct comparison go, to know the areas of the evaporating and condensing surfaces nor the term due to the rate of diffusion. Mr. Parker has kindly made one set of determinations for me at constant temperature to show that under uniform conditions one actually gets a constant reaction-velocity. The salt taken was ammonium chloride, and the temperature was 35°. The results are given in Table I. The last determination was made when the solution was no longer saturated, all the salt having been dissolved. As was to be expected, the rate of condensation has decreased, owing to the increased vapor-pressure of the solution.

TABLE I.

No. of hours.	Gain per hour.	No. of hours.	Gain per hour.
24	0.039 g.	49	0.044 g.
25	0.040	23	0.041
71	0.036	25	0.042
48	0.042	24	0.042
71	0.042	25	0.031

The results agree as well as one could wish under the circumstances. It would doubtless be possible to get more accurate results by stirring the solution so that there should be no differences of concentration in the liquid. This method gives an easy and fairly accurate measurement of vapor-pressures of salt solutions, and I hope before long to communicate some interesting applications of it.

We are now able to state the conditions under which deliquescence will take place. An anhydrous salt is permanent if the concentration of the water-vapor is equal to or less than the vapor-pressure of its saturated solution. It is deliquescent if the pressure exceeds that value. With hydrated salts the case is a little different, because they can also lose water. It is well known that below a certain pressure of water-vapor they effloresce. If the concentration of water in the vapor space becomes greater than that corresponding to the saturated solution, they will deliquesce. Do these two concentrations coincide, or is there an interval over which the salt is permanent and in indifferent equilibrium with the vapor? In other words, does a hydrated salt have the same vapor-pressure as the solution with which it is in equilibrium? I have been unable to find any definite statement on the subject in the text-books of Ostwald or of Nernst; but the impression which I get from their writings is that they would probably apply the law of the Substitution of Phases to this case, and would say that the two phases, hydrated crystals and saturated solution, being in equilibrium with each other, must have the same vapor-pressure.[1] I am the more inclined to believe that this is a fair statement of

[1] Cf. Zeitschr. f. phys. Chem., 1, p. 205, 1887.

their views, because there is no question but that Planck holds this view. He says:[1] "All coexisting solid and liquid phases send out the same vapor." This is the more remarkable because there is abundant evidence that this is not true. Van 't Hoff[2] has shown that slightly effloresced sodium sulfate has a less vapor-pressure than the saturated solution; Roozeboom[3] has stated that the solution and the hydrate cannot have the same vapor-pressure except at the inversion temperature; and Lescœur, while disputing the accuracy of Roozeboom's generalization, brings forward a long series of observations to show that it is true in a great many cases. In Table II. I tabulate some of Lescœur's measurements on the vapor-pressures of hydrated salts and their saturated solutions.[4] It will be noticed that the differences between the two are often enormous. The pressures are given in millimeters of mercury; the temperature is 20°.

TABLE II.

	Pressure in mm. Hg.			Pressure in mm. Hg.	
	Solution.	Salt.		Solution.	Salt.
$CaCl_2\ 6\ H_2O$	5.4	2.3	$Na_2CO_3\ 12\ H_2O$	16.0	10.1
$SrCl_2\ 6\ H_2O$	11.4	5.6	$Na_2SO_4\ 10\ H_2O$	15.7	13.9
$MnCl_2\ 4\ H_2O$	8.0	3.8	$Na_2SO_4\ 7\ H_2O$	15.0	10.5
$NiCl_2\ 6\ H_2O$	8.0	4.6	$MgSO_4\ 7\ H_2O$	14.5	7.3
$CoCl_2\ 6\ H_2O$	9.0	4.0	$CuSO_4\ 5\ H_2O$	58.0	30.0
$NaBr\ 4\ H_2O$	9.6	7.6	$MgCl_2\ 6\ H_2O$	5.7	1.8
$SrBr_2\ 6\ H_2O$	9.1	1.7	$NaI\ 4\ H_2O$	5.4	1.5

It is generally assumed that two phases in equilibrium must give off the same vapor, or that it would be possible to make a perpetual motion machine, but this conclusion is not necessary. Suppose we have a system composed of hydrated salt, solution, and vapor. If the solution has a greater vapor-pressure than the

[1] Grundriss d. Thermochemie, p. 125.
[2] Zeitschr. f. phys. Chem., 1, p. 185, 1887.
[3] C. r. 110, p. 134, 1890.
[4] Ann. chim. phys. (6), 19, p. 533, 21, p. 511, 1890; (7), 2, p. 78, 1894.

hydrated salt, there will be a tendency for water to precipitate on the crystals; but the effect of this will be to cause some of the salt to go into solution, and at the same time water will evaporate to restore the vapor-pressure of the saturated solution, precipitating the same quantity of salt which has just dissolved. No change has taken place in the system, and there is no surplus energy with which to run a machine. The matter can be seen even more clearly in the limiting case, that of an anhydrous salt in equilibrium with a saturated solution and the vapor thereof. Here there can be no question that we have a solid and a liquid phase coexisting, and that they do not give off the same vapor. With calcium chloride, and still more strikingly with the hydrates of ferric chloride, Roozeboom[1] has shown that the same hydrate can be in stable equilibrium with two different solutions, one containing more water than the crystals, the other less. As the vapor-pressures of the two solutions are not the same, it follows that at least one is different from the value for the hydrated salt, which is sufficient to prove the point. The case does not rest on this alone. We may reach the same conclusion in another way. If we add to a saturated solution of a hydrated salt a second salt having different ions, we shall have more of the first salt go into solution. The solution will now have a less vapor-pressure than before. If the vapor-pressure of the hydrated salt had been equal to the vapor-pressure of its saturated solution, it would be greater than that of the new solution, and the crystals would effloresce, no matter how small the added quantity of the second salt was. In general this is not the case, and I conclude that the vapor-pressure of a hydrated salt is not necessarily the same as that of the solution with which it is in equilibrium. It has been overlooked by every one except Roozeboom and van 't Hoff that in the system, salt, solution, and vapor, there are two kinds of equilibrium represented, the stable and the indifferent. A given solution can have only one vapor-pressure at a given temperature; the concentration of water vapor in equilibrium with an anhydrous or a hydrated salt may have any value between two limits. The reason for this difference is that the concentration of the solution can

[1] Zeitschr. f. phys. Chem., 4, p. 34, 1889; *Ibid.*, 10, p. 486, 1892.

vary continuously, that of the hydrate cannot. The vapor-pressure of a system containing hydrate, water vapor, and a third phase will depend therefore on the nature of the third phase. The experiments of Roozeboom[1] show that this is so.[2] In Table III. I give his determinations of the vapor-pressures at which $CaCl_2\,6\,H_2O$ is in equilibrium with different phases, the pressures being in millimeters of mercury.

TABLE III.

Temperature.	0°	10°	20°	25°
$CaCl_2\,6\,H_2O$, solution, vapor . . .	1.944	3.456	5.616	6.696
$CaCl_2\,6\,H_2O$, $CaCl_2\,4\,H_2O\alpha$, vapor .	0.92	1.92	3.78	5.08
$CaCl_2\,6\,H_2O$, $CaCl_2\,4\,H_2O\beta$, vapor .	0.76	1.62	3.15	4.32

As will be seen, not only is the vapor-pressure of the saturated solution different from that when there is a solid phase present, but there is a marked difference between the values for the systems $CaCl_2\,6\,H_2O$, $CaCl_2\,4\,H_2O\alpha$, vapor, and $CaCl_2\,6\,H_2O$, $CaCl_2\,4\,H_2O\beta$, vapor. This discrepancy is a real one, being greater than the probable error of the measurements. The question suggests itself, in view of these facts, whether it is proper to speak of the vapor-pressure of a hydrated salt; in other words, whether it has a true vapor-pressure independent of the nature of the third phase. There is such a value as we may see from the following considerations: Suppose that water and the salt under consideration could form a continuous series of mix crystals, as is the case with the alums. For a given temperature and a given concentration of the solid phase the pressure would be definitely fixed, just as is the case when the equilibrium is between a liquid solution and its vapor. That value is the true vapor-pressure of that crystal. If we bring in discontinuity, we increase the range of pressures at which the hydrate can be in equilibrium, but we do not change the fact that one particular pressure differs from the others, because the equilibrium in that case is independent of the discontinuity in the solid phase. I define the true vapor-

[1] Zeitschr. f. Chem., 4, p. 42, 1889.

[2] This has been overlooked by Nernst, Theor. Chem., p. 491.

pressure of a given hydrate at a given temperature as the pressure at which it would be in equilibrium if it were one term in a continuous series of mix crystals. This is probably the same as the vapor-pressure of the system containing hydrate, anhydrous salt, or lower hydrate, solution, and vapor in equilibrium, the number of the components in the solution not being limited.[1] If this be true, it follows that as yet only in the cases where the measurement has been made at the inversion temperature can we be sure that we have determined the true vapor-pressure of the hydrated salt, for there is no reason to assume that this value coincides with that usually measured for the equilibrium between hydrate, effloresced product, and vapor.

The fact that the saturated solution often has a greater vapor-pressure than the hydrated salt which crystallizes from it is of great interest as throwing light on some of the peculiarities which have been discovered in regard to the inversion temperature of salts. It is clear that if we add to a saturated solution enough of any substance to bring the vapor-pressure of the solution below that of the hydrated salt in respect to which the solution is saturated, the salt must effloresce. The simplest way to do this is to add a salt having no common ion. The only instance of this which I can now recall is the case cited by Meyerhoffer,[2] that the double salt $CuCl_2KCl$ crystallizes out of solutions containing acetic acid, instead of the double salt, $CuCl_2\ 2\ KCl\ 2\ H_2O$. As I shall have occasion to discuss the mechanism of this reaction more fully under another head, I will only point out that the hydrated double salt ceases to be stable as soon as, by the addition of acetic acid, the partial pressure of the water-vapor in equilibrium with the solution becomes less than the true vapor-pressure of the hydrated double salt. That this instance might not seem an isolated, abnormal case, I have made a few qualitative experiments on other hydrated salts, and have found the phenomenon to be entirely general.

Another means of obtaining the same result, namely dehydration, is to add a substance which increases the number of re-

[1] Cf. Vriens, Zeitschr. f. phys. Chem., 7, p. 208, 1891.

[2] Zeitschr. f. phys. Chem., 3, p. 339, 1889.

acting weights in solution, though decreasing the solubility of the hydrated salt. This effect may be produced by a non-electrolyte in which the salt is insoluble, or by a salt having a common ion, though it by no means follows that either of these must do it. The dehydrating effect of alcohol on many salts with water of crystallization is too familiar to need more than a reference. That salts crystallize in a more or less completely dehydrated condition from solutions containing an excess of acid is also well known. This has been used as a method for obtaining salts having less crystal water than is normal at the temperature of the experiment.[1] This means that the inversion temperature of that particular hydrate in respect to the solution has been changed, and this phenomenon has been noticed often without any very satisfactory explanation having been given. The reaction

$$MgSO_4\,7\,H_2O = MgSO_4\,6\,H_2O + H_2O$$

takes place at 48°.2 when no other salt is present; at 47°.2,[2] if an excess of $K_2Mg(SO_4)_2\,6\,H_2O$ be present, and at 29°.8,[3] if the solution be also saturated in respect to potassium chloride. Loewenherz[4] has noticed that the inversion temperature is lowered to 25° if, to a saturated solution of magnesium sulfate, magnesium chloride be added in such quantities that the solution contains 73 units of anhydrous magnesium chloride to 1000 units of water, or if magnesium chloride and potassium chloride be added in such proportions as to give concentration of 62 units of $MgCl_2$ and 16 units of KCl per 1000 units of water. We have in all these cases the same phenomenon, addition of another salt or salts reducing the vapor-pressure of the solution below that of the hydrated salt, which thereupon effloresces. The difference in the effect produced by magnesium chloride and by Schönite is due chiefly to the greater solubility of the former, though the relative influence on the solubility of the magnesium sulfate is also a factor. The change of Schönite into potassium astrakanite, corresponding to the reaction

$$K_2Mg(SO_4)_2\,6\,H_2O = K_2Mg(SO_4)_2\,4\,H_2O + 2\,H_2O,$$

[1] Cf. Ditte, Ann. chim. phys. (5), 22, p. 560.
[2] Zeitschr. f. phys. Chem., 12, p. 426, 1893.
[3] *Ibid.*, 13, p. 489, 1894.
[4] *Ibid.*, 13, p. 480, 1894.

occurs at 92° if there is an excess of potassium sulfate present, and at 72° in presence of an excess of the magnesium sulfate with six units of water.[1] If the solution is not saturated in respect to $MgCl_2\,6\,H_2O$, the inversion temperature may be made to lie anywhere between these two temperatures, depending on the amount of magnesium sulfate in solution. There is no doubt in my mind that still other inversion temperatures could be found by adding other salts to a saturated solution of Schönite. As is well known, $Na_2SO_4\,10\,H_2O$ changes into the anhydrous salt at about 33° if there is nothing else in solution. If an excess of

$$Na_2Mg(SO_4)_2\,4\,H_2O$$

be added, the inversion temperature falls to 26°, while an excess of NaCl and $MgSO_4\,7\,H_2O$ carries it down to 15°.[2] The double salts of copper and potassium chlorides have been studied by Meyerhoffer,[3] who found that the reaction which takes place is represented by the equation

$$CuCl_2\,2\,KCl\,2\,H_2O = CuCl_2KCl + KCl + 2\,H_2O.$$

This change takes place at 92° if the solution is saturated in respect to KCl; at 55° if saturated in respect to $CuCl_2\,2\,H_2O$. Here, as before, the greater solubility of the cupric chloride is the cause of this change in the stability of the hydrated double salt. This reaction differs from the others which we have considered in that we do not get a simple case of dehydration as we should expect, but have the formation of a new salt with separation of potassium chloride. The reason for this seems to be that the anhydrous salt $CuCl_2\,2\,KCl$ is unstable and goes over into the form $CuCl_2KCl$ and KCl. Why this should be so is not known. I have let the blue double salt effloresce over strong sulfuric acid, but the product seems to be the red double salt and potassium chloride. It would be very interesting to know whether double salts of this type, where the two components are held together by the water of crystallization, differ in any other properties from hydrated double salts which do not show this peculiarity.

[1] Zeitschr. f. phys. Chem., 12, p. 417, 1893.
[2] *Ibid.*, 1, p. 176, 1887.
[3] *Ibid.*, 3, p. 336, 1889.

The cases which we have examined so far have all been alike in one respect, that the hydrated salt which it was proposed to make effloresce was stable below the inversion temperature. This is not necessary, and in astrakanite we have the reverse order of things.

$$MgSO_4\,7\,H_2O + Na_2SO_4\,10\,H_2O = Na_2Mg(SO_4)_2\,4\,H_2O + 13\,H_2O.$$

Here the double sulfate crystallizes out above 21°.5, the single salts below that temperature. Adding a salt which will increase the number of ions in solution will therefore raise the inversion temperature, while the addition of a salt which decreases the number of ions will lower it. In other words, we shall have our previous effects reversed. Both these cases have been realized by van 't Hoff.[1] In the presence of an excess of $MgCl_2\,6\,H_2O$ the inversion temperature is raised to 31°, while saturating the solution with sodium chloride produces the opposite effect, the inversion temperature becoming +5°. For the first time we get a marked effect, due to the different precipitating power of two salts. The addition of either magnesium or sodium chloride should cause a decrease in the solubility of the double salt; but in the first case the precipitation is so slight that the number of ions in solution is increased, and in the second it is so great that the vapor-pressure of the solution rises.

Having shown that in general the vapor-pressure of a partially effloresced salt is less than that of its saturated solution, it is worth while to consider whether the two can be equal except at the inversion temperature. In Table IV. I give some of Lescœur's measurements.[2] The pressures are in millimeters of mercury.

[1] Zeitschr. f. phys. Chem., 1, pp. 170, 176, 183, 1887.
[2] Ann. chim. phys., (7), 2, p. 78, 1894.

TABLE IV.

	Pressure.		Temperature.
	Solution.	Salt.	
$BaBr_2\ 2\ H_2O$	10.7	10.6	20°
$BaBr_2\ 2\ H_2O$	124.0	124.0	60°
$MgBr_2\ 6\ H_2O$	3.4	3.3	20°
$MgBr_2\ 6\ H_2O$	166.0	166.0	100°
$CdBr_2\ 4\ H_2O$	10.0	9.0	20°
$CdBr_2\ 4\ H_2O$	122.0	124.0	60°
$BaI_2\ 6\ H_2O$	8.4	8.4	20°
$BaI_2\ 6\ H_2O$	58.0	60.0	60°
$MnBr_2\ 4\ H_2O$	5.0	5.0	20°
$MnBr_2\ 4\ H_2O$	202.0	200.0	100°

We have in all these cases equality between the two vapor-pressures, and that over a considerable range of temperature. A more interesting confirmation is furnished by Joannis[1] in his measurements of the vapor-pressure of saturated solutions of sodammonium and of the partially effloresced product.

TABLE V.

	Pressure.	Temperature.
1 g. NH_3Na + 1.669 g. NH_3	169.7 mm.	0°
1 g. NH_3Na + 0.460 g. NH_3	169.7	0°
0.971 g. NH_3Na + 0.029 g. Na	169.7	0°
0.487 g. NH_3Na + 0.513 g. Na	169.7	0°
0.108 g. NH_3Na + 0.892 g. Na	169.7	0°
0.043 g. NH_3Na + 0.957 g. Na	169.65	0°
1 g. NH_3Na + 0.46 g. NH_3	117.0	− 10°
0.7 g. NH_3Na + 0.30 g. Na	117.3	− 10°
0.39 g. NH_3Na + 0.61 g. Na	117.0	− 10°
0.19 g. NH_3Na + 0.81 g. Na	117.1	− 10°

The agreement is perfect, and as the compound is stable at +22°, the objection of Roozeboom that the measurements had been made in the neighborhood of the inversion temperature

[1] C. r., 110, p. 238, 1890.

cannot be sustained. I see at present no theoretical reason why the dissociation-pressure of a hydrated salt may not be the same as that of its saturated solution, and I do not agree with Roozeboom when, after describing the usual diagram for the equilibrium between different hydrates and water, he says:[1] "Il en resulte que la tension de dissociation est toujours plus petite que celle de sa solution saturée, sauf dans le point C. Ainsi ce point represente la température et la pression unique ou il y a coexistence des deux corps solides avec la solution et la vapeur d'eau." At the inversion temperature there come together three vapor-pressures,[2] that of the hydrate, of its saturated solution, and of the saturated solution of the anhydrous salt, and all that can be predicted is that the vapor-pressure of the stable saturated solution is greater than that of the solution saturated in respect to the labile modification. How rapidly the curves for the true vapor-pressure of the hydrate and its saturated solution diverge, or whether they necessarily diverge at all, is a question which has no bearing on the inversion temperature. They may intersect before the inversion temperature is reached, in which case the salt melts and there is no formation of a new solid phase.

In speaking of the stable and the labile modifications, it must be kept in mind that these terms are to be reversed if we are considering the vapor-phase. When we refer to the solution, the more stable modification is the less soluble one. When we refer to the vapor-phase, it is the one having the lesser vapor-pressure. Below 33°, for instance, the saturated solution of anhydrous sodium sulfate has a smaller vapor-pressure[3] than the solution in equilibrium with the hydrated salt, and is therefore more stable in that respect. If we place the two saturated solutions in the two limbs of an inverted U-tube, water will distill from the one containing the hydrated salt into the other. We can go still further, and

[1] C. r., 110, p. 135, 1890.

[2] If there are no other components, the dissociation curve intersects here. The true vapor-pressure of the hydrate will always lie between the pressure of the saturated solution and the dissociation pressure.

[3] Meyerhoffer's diagram is wrong. (Phasenregel, p. 28.) His curves for the vapor-pressures of Na_2SO_4, solution, vapor, and of $Na_2SO_4\,10\,H_2O$, solution, vapor, if continued so as to represent the labile equilibria, are in contradiction with the facts.

say that if the system hydrated salt, anhydrous salt, vapor, has a greater vapor-pressure than the system anhydrous salt, solution, vapor, the hydrated salt will effloresce, and the water will condense in the beaker containing the saturated solution of the anhydrous salt. We shall thus have the spontaneous formation of the less stable system at the expense of the more stable. I tried to realize this with sodium sulfate at a temperature of about thirty degrees, and it looked once as if I had succeeded, but I cannot be certain of this. The great difficulty in carrying out the experiment is, of course, the spontaneous appearance of the more stable modification in the solution. It may be that this experiment is theoretically impossible for the reason that the vapor-pressure of the system hydrate, anhydrous salt, vapor, may be necessarily less than that of the saturated solution of the unstable modification. This is the case with the saturated solutions of $CaCl_2 4 H_2O\alpha$ and $CaCl_2 4 H_2O\beta$.[1] This would be very interesting if true. In that case Roozeboom would be entirely correct in the remarks of his which I have just quoted. While this may be true, it has not yet been shown by any one so far as I am aware.

While I was in Amsterdam, Professor van 't Hoff showed me a very pretty lecture experiment which consisted in putting clear pieces of crystallized calcium sulfate in mixtures of sulfuric acid and water of different proportions. In the solutions containing much sulfuric acid, the crystals became cloudy, and in those containing much water they remained clear. The concentration at which the first dehydration took place could be determined with great accuracy by the eye. The method in this form is adapted only to sulfates insoluble in water, and is therefore incapable of general application. This is easily remedied by bringing the crystals in contact with the vapor of the solution instead of with the liquid itself. In this way one can use any salt which forms clear crystals, and one can equally use any other drying agent. Theoretically there are objections to be made. For instance, it would not be proper to say that with sodium carbonate there was no formation of sodium sulfate; but this reaction runs so slowly that the experiment is ended long before this effect becomes noticeable.

[1] Zeitschr. f. phys. Chem., 4, p. 43, 1889.

This might not be the case were one to use strong hydrochloric acid as the drying agent. I have made a few measurements on copper and magnesium sulfates with rather surprising results. Frowein[1] found the vapor-pressure of partially effloresced copper sulfate to be equal to 10.9 mm. of mercury at 30°.2; I find that copper sulfate just begins to effloresce when placed over a solution containing 48 per cent of sulfuric acid by weight, the temperature being 30°. This corresponds to a vapor-pressure of about 13 mm.[2] of mercury, or over two millimeters more than the value found by Frowein. This is beyond the limits of experimental error, as my measurements are accurate to within one-half a per cent of H_2SO_4, while the value of 10.9 mm. corresponds to a solution containing 51.5 per cent of sulfuric acid by weight. The same thing was noticed with magnesium sulfate. At 30°, Frowein's measurements give for the vapor-pressure of partially effloresced $MgSO_4\,7\,H_2O$ the value (by interpolation) of 17.5 mm. Hg corresponding to the vapor-pressure of a solution containing 40.7 per cent HSO by weight. The direct experiment shows that magnesium sulfate effloresces over a 38 per cent solution of sulfuric acid, which has a vapor-pressure of 19.2 mm. As the vapor-pressure of an 84.5 per cent solution is only about 0.23 mm. at 30°, there is no appreciable error in assuming the whole vapor-pressure of sulfuric acid solutions at that temperature to be due to water-vapor. The experiments just cited force upon us the conclusion that the equilibrium between a hydrated salt and water-vapor is affected by the presence of other substances. This shows that the minute quantity of sulfuric acid present as vapor does not behave as a so-called "indifferent" gas, and the same will be true of alcohol vapor and of the vapors of all substances capable of forming a solution with water at that temperature of the experiment. This has never been recognized. Nernst[3] says: "Haben wir das Gleichgewicht zwischen Wasserdampf und wasserhaltigem Aether einmal untersucht, so ergibt umgekehrt die Bestimmung der Wassermenge, die einem krystallwasserhaltigen Salze von Aether entzogen wird, die Dissociationsspannung des Salzes."

[1] Zeitschr. f. phys. Chem., 1, p. 5, 1887.

[2] Landolt and Börnstein's Tables, p. 65.

[3] Theoretische Chemie., p. 524.

Linebarger[1] has based a method of measuring vapor-pressures on this.

This method can give good results only in cases where the effects due to the other liquid fall within the experimental error. This seems to be the case with ether, which is not surprising, though I have little doubt that a careful series of determinations would show that the results from the indirect method were larger than those by direct measurement. This would certainly be the case if alcohol or methyl alcohol were taken.[2] The importance of this is that we can no longer assume that the same amount of work is done in compressing a given quantity of water-vapor from one volume to another in the two cases when we have the water-vapor alone and when we have alcohol-vapor present also, but work with a piston permeable to alcohol.

Since it is not necessarily true that a solid and a liquid phase when in equilibrium must have the same vapor-pressure, it seems worth while to ask whether two liquid layers in equilibrium must give off the same vapor. Ostwald has given a proof of Konowalow's Law, which I quote:[3] "Denken wir uns nämlich einen ringförmigen Hohlraum, Fig. 1, der bei *A* etwa eine gesättigte Lösung von Wasser in Äther, bei *B* eine solche von Äther und Wasser und in *C* den Dampf der Flüssigkeiten enthalte, so würde, falls der Dampf über *A* eine andere Spannung als bei *B* hätte, oder anders zusammengesetzt wäre, eine fortdauernde Destillation oder Diffusion von der einen Seite zur anderen stattfinden, ohne dass jemals ein Stillstand einträte, da auch die Flüssigkeiten sich durch Diffusion immer wieder ausgleichen würden. Wir hätten also ein Perpetuum mobile was unmöglich ist." This sounds most convincing; but let us examine this so-called "perpetuum mobile" a little more closely. For the purposes of argument, let us assume that the vapor given off by the ether layer contains more ether than the vapor given off by the water layer and that the second vapor contains more water than the first. Ether will therefore

[1] Zeitschr. f. phys. Chem., 13, p. 500, 1894.

[2] I ventured to point out to Mr. Linebarger, nearly a year ago, this source of error; but he replied that the reasoning on which the method was based was free from hypothesis and as certain as the laws of thermodynamics.

[3] Lehrbuch, I., p. 644.

distill from *A* to *B*, and water from *B* to *A*. The water condensing at *A* will sink through the less dense ether layer; the ether which condenses at *B* will become saturated with water, and we shall have as the second step in the process three liquid layers, the solution of water in ether at *A*, the solution of ether in water at *B*, and an infinitely thin film of a solution of water in ether on top of the aqueous layer. Both free surfaces having the same composition, there is no need nor possibility of any further distillation if we neglect the effect due to gravity.[1] In other words, it is conceivable that we may have two liquid layers with different vapor-pressures and not assume the possibility of a perpetual-motion machine. Whether such a case really exists is an experimental problem, for which there are as yet no data. It is true that two liquid layers such as benzol and water, ether and water, have different boiling points, but this evidence is capable of another interpretation and is not conclusive. Of course, if it is shown that two liquid layers do not, as a rule, have the same vapor-pressure, that part of my argument on the difference between solvent and solute, which is based on the contrary assumption,[2] falls to the ground.

The results of this paper, most of which are contained implicitly or explicitly in Roozeboom's articles, may be summed up:

(1) Anhydrous salts are permanent till the pressure of the water-vapor in the gaseous phase becomes greater than the vapor-pressure of the saturated solution, after which they deliquesce.

(2) Hydrated salts deliquesce when the pressure of the water-vapor becomes greater than the vapor-pressure of the saturated solution, effloresce when it becomes less than the vapor-pressure of the system containing hydrated and anhydrous salt, and are permanent when the value lies between these limits.

(3) The vapor-pressure of a hydrated salt is usually less than the vapor-pressure of its saturated solution.

[1] Professor Trevor pointed out to me some time ago that, assuming the two liquid layers had the same vapor-pressure when at the same level, the effect of gravity would cause distillation till the system was symmetrical and the two free surfaces at the same level. This experiment has since been tried in his laboratory with the predicted result.

[2] PHYSICAL REVIEW, III., p. 203, 1895.

(4) The vapor-pressure of a hydrated salt is affected by the nature of the effloresced salt.

(5) The true vapor-pressure of a hydrated salt is probably known in few cases.

(6) The equilibrium between a hydrated salt and water-vapor is affected by the presence of sulfuric acid.

(7) Two liquid layers in equilibrium need not have the same vapor-pressure.

May 1, 1895.

ON THE HEAT EFFECT OF MIXING LIQUIDS.

BY C. E. LINEBARGER.

Introductory.

THE wide-reaching analogy between gases and solutions, first clearly pointed out by van 't Hoff, has proven very fruitful when applied to the elucidation of the phenomena presented by solutions. The fact that the laws which have been established for gaseous matter are by a little extension applicable to dissolved matter has been of great service in getting at the nature of solution. While these laws are strictly true for gaseous and dissolved matter only in states of great rarefaction or dilution, they may, when properly modified, be employed in the investigation of gases or solutions of any degree of condensation. Especially is this true in the case of such substances as do not suffer molecular polymerization, for the complexity caused by the introduction of considerations relative to the association and dissociation of the molecules is in such cases not present. In the case of normal liquids, a close continuity may be expected, not only in the passage from the liquid to the gaseous state, but also in the properties of the two states, and such differences as may be found in the liquid state compared with the gaseous state may be accounted for by comparatively simple assumptions.

An important property of different portions of matter is their possible inter-diffusibility or miscibility with one another. A characteristic of the gaseous state is unlimited miscibility. All liquids which do not suffer any alteration in the size of their molecules on passing into the gaseous condition are also perfectly miscible; at least, no exception to this statement, so far as I know, has yet been found. Many associated liquids, however, do not mix in all proportions under certain conditions, but a certain degree of miscibility may always be observed, which, through

changes in temperature and pressure, may become perfect. Solids, also, are not generally found to be capable of forming homogeneous mixtures under ordinary conditions; yet by suitable changes of these conditions, it is probable that they may be made to mix. Van der Waal's law — "All substances can mix with one another if subjected to sufficient pressure"[1] — is without doubt true of any system of bodies whatever, no matter what their state of aggregation; seeming contradictions must, and doubtless will, be cleared away by future experimentation.

To mix substances requires energy. The kinds of energy expended in effecting the mixing are principally heat, volume, and chemical energy; in the case of liquids and solids, surface and osmotic energy also come into play; in all but exceptional cases electrical energy and light energy play no part. When the sum of the volumes of the unmixed substances is equal to the volume of the mixture, the mechanical energy, which is mainly evident in the overcoming of the pressure of the atmosphere, is equal to zero, and in many cases the changes of volume that occur during the mixing are so slight that the concomitant changes of mechanical energy vanish in comparison with the quantities of other kinds of energy brought into action. Heat energy plays by far the most important *rôle* in the mixing of substances.

In nearly all work, both experimental and theoretical, on the heat changes occurring during solution, materials have been employed which can exhibit the phenomenon of saturation or a limited degree of miscibility, and only one side of the question is taken into account. In the case of aqueous solutions of salts, which have as yet received the most attention, the solution of the salt in the water is alone thought of, although it is just as proper to say that the water dissolves in the salt, as that the salt dissolves in the water. This view of the subject is probably due to the circumstance that the salt alone undergoes a change in its state of aggregation; it *becomes* liquid, while the water *remains* liquid. But in reality solution is just as truly reciprocal in this case as in the case of dissolving liquids in liquids. This last-named phenomenon

[1] Die Continuität des gasförmigen und flüssigen Zustandes. Roth's German translation, p. 146.

—solution of liquids—has received but little attention, especially when the liquids are normal. But as normal liquids approximate closely to gases in their behavior, and as gases present the simplest phenomena, it may be expected that investigation of the thermal behavior of normal liquids will yield the simplest possible results, and give some indications as to the best means of getting a clear understanding of the general question of solution.

The object of this paper is, accordingly, the determination and discussion of the heat effect of mixing normal liquids.

Historical.

H. Sainte-Claire Deville[1] determined the "heat produced by twenty-five different mixtures of water and sulphuric acid." No experimental details are given, and the method employed is incapable of giving very accurate results. Deville believed that his data were in corroboration of certain theoretical views that he advanced, and, when the latter were subjected to some animadversions on the part of Jamin,[2] he protested energetically.[3] To this, Jamin[4] made a rather detailed reply, giving some experimental determinations of the changes of temperature occurring when alcohol and water are mixed, as corroborative of a theory of his own in contradiction to that of Sainte-Claire Deville. Still the latter was not convinced, and maintained his old opinions.[5] It is not necessary to enter into the consideration of the theoretical views advanced by these two scientists, as none of them have proven to be correct.

Favre[6] determined, by the mercury calorimeter, the heat effect of mixing, in several proportions, water with sulphuric acid, with alcohol, with acetic acid, and with glycerine; alcohol with glycerine, and with acetic acid; and acetic acid with sulphuric acid. His results showed that, in the mixing of these liquids, heat was either evolved or absorbed. As he puts it, having, as he did, the idea that solution was an example of a kind of chemical affinity: "Deux ordres d'actions semblent se produire simultanément et marcher de front; une action d'attraction réciproque des molecules hétéro-

[1] Comptes Rendus, 50, p. 534, 1860.
[2] *Ibid.*, 70, p. 1309, 1870.
[3] *Ibid.*, 70, p. 1379, 1870.
[4] *Ibid.*, 71, p. 23, 1870.
[5] *Ibid.*, 71, p. 30, 1870.
[6] *Ibid.*, 50, p. 1150, 1860, and 51, p. 316, 1860.

gênes qui sont mises en contact et qui est accompagné d'un degagement de chaleur, et une action de diffusion qui produit un abaissement de température. Le nombre fourni par l'expérience est positive ou negative suivant que la première ou la seconde de ces actions predomine." His data cannot be well compared with later ones, as he has omitted to give the details necessary for a reliable comparison.

Bussy and Buignet[1] determined the changes of temperature brought about by mixing, in various proportions, alcohol with carbon bisulphide, chloroform, ether, and essence of terebenthine; water with acetic acid, and alcohol; ether with carbon bisulphide, essence of terebenthine, and chloroform; and carbon bisulphide with essence of terebenthine. The results of their experiments are similar to those obtained by Favre,[2] although his researches are not mentioned. This induced Favre[3] to call attention to his work, and, in so doing, to communicate some new results on the thermal effect of mixing water with methyl alcohol, and of mixing ethyl alcohol with methyl, amyl, and caprylic alcohols, as well as glycol. This claim of priority was recognized by Bussy,[4] who stated that he had been ignorant of the work by Favre, but that, anyhow, he had taken different liquids, of a simpler nature than Favre had.

In a subsequent paper, Bussy and Buignet[5] determined the specific heats of many of the mixtures, the change of temperature caused by the mixing of which they had previously observed,[6] thus permitting the calculation in heat units of the thermal effect.

Guthrie[7] determined, by rather a crude method, the changes of temperature occasioned by mixing alcohol with ether, carbon bisulphide, chloroform, and benzene; ether with carbon bisulphide, amylene, chloroform, and benzene; carbon bisulphide with amylene, chloroform, and benzene; amylene with chloroform, and benzene; and chloroform with benzene. The changes in the volume of these liquids, when mixed, were also measured, it being found that, when the mixing was accompanied with a rise of temperature,

[1] Comptes Rendus, 59, p. 673, 1864, and Annales de chimie et de physique, (4), 4, p. 1, 1865.

[2] *loc. cit.*

[3] Comptes Rendus, 59, p. 783, 1864.

[4] *Ibid.*, 59, p. 785, 1864.

[5] *Ibid.*, 64, p. 330, 1867.

[6] *loc. cit.*

[7] Philosophical Magazine, (5), 18, p. 495, 1884.

contraction in volume occurred, while, when there was a fall in temperature, expansion took place. These generalizations are, however, based on too narrow a field of inquiry, and Guthrie's paper contains very little that is really novel, at least, along these lines.

W. Alexejew,[1] in summing up his work on the solubility of liquids in liquids, communicates some data as to the amount of heat absorbed in mixing benzene and aniline in several proportions. This he finds to be quite insignificant, and states in this connection: "Für ein Gemisch von 68.5 Proc. Benzol und 31.5 Toluol bei 14°, z. B. ist sie gleich −13.7 cal." As he states later that the possible error of a determination may amount to 5 cal., and as he does not give the absolute masses of the liquids taken, the absorption of heat given by him for this case may even be less than −8.7 cal.

Experimental Details.

Of the common methods of carrying out thermochemical measurements, the one in which use is made of a Bunsen's ice calorimeter has been preferred, mainly for the reasons that accurate results can be obtained with small quantities of material, and because it is unnecessary to know the specific heats of the liquids mixed.

The ice calorimeter employed was of rather large size, permitting of the introduction of about 15 c.c. of liquid. The amount of mercury expelled or drawn into the outer chamber by the formation or melting of ice was determined by weighing, as recommended by Schüller and Wartha;[2] indeed, the disposition of the apparatus was very similar to that adopted by these investigators, there being an outer cylindrical vessel filled with pure water, around the walls of which was a layer of ice, etc. The calorimeter was set in an ice box, and covered, with the exception of the top of the inner tube and the mercury tube, with clean snow or ice. The room in which the work was done was nearly all the time at the temperature of freezing water, and the temperature never rose above 5° or 6°.

After the calorimeter had been brought into normal working condition, it was found that the mercury was continually moving

[1] Wiedemann's Annalen, 28, p. 322. [2] *Ibid.*, 2, p. 359, 1877.

in one direction or the other, according to external conditions. As the amounts of heat evolved or absorbed by the mixing of non-associated liquids are generally quite small, it was necessary to keep strict account of this movement of the mercury; as the degree and direction of the movement changed very slightly in intervals of time long in comparison with the time occupied for the performance of an experiment, this could be done both easily and accurately in a way to be described later.

The cooling of the liquids to 0°, and their subsequent mixing, was accomplished as follows: A thin glass tube, closed at one end, and of such external diameter as to permit of its being slipped easily, but snugly, into the inner tube of the calorimeter, was taken of such length that about an inch of it projected out of the calorimetric tube. A pipette fitting easily into the above tube had its outlet directly below its cylindrical bulb, and was closed by means of a glass rod running axially up through the pipette and ground accurately into the outlet. A bit of thin rubber tubing was slipped over this glass rod and pushed down between the upper stem of the pipette and the rod, thus closing the pipette above. By means of a good cork the pipette was held within the tube mentioned at the beginning of this paragraph.

A rectangular piece of aluminium foil was for about two-thirds of its length cut into in several places on each side to near the middle, and the parts thus formed were so bent that, when the uncut portion of the foil was rolled into cylindrical shape and slipped over the lower part of the bulb of the pipette, where it was held securely by its own elasticity, they formed a number of small paddles, some directed upwards and some downwards. This stirring device proved to be very efficient, the mixing of two liquids being brought about rapidly and perfectly.

To make a determination, a certain amount of one liquid was drawn up into the pipette and weighed to 0.0001 gram. The other liquid was weighed in the tube, which was corked during the operation. The aluminium stirring contrivance was then slipped over the bulb of the pipette, and the latter passed into the tube, where it was held in place by a tightly fitting cork, and was so adjusted that its orifice would be above the level of the liquid after

the mixing had been done, while the paddles reached to the bottom of the tube.

A weighed dish of mercury was always placed to catch the expelled mercury for exactly half an hour just before the tube and pipette with their contents were placed in the inner tube of the calorimeter; in this way a calorimeter correction was obtained just before the performance of an experiment. The weighed dish of mercury was then exchanged for an unweighed one, and the tube and pipette which had been standing in the ice box, so that they had already attained the temperature of 0°, were placed in the calorimetric chamber. In a half-hour or so a weighed dish of mercury was placed under the mercury tube, and the amount of mercury moved during another half-hour determined. Again a weighed dish of mercury was placed in position, and without delay the cork holding the pipette was lifted a little and its contents made to run out into the tube. The pipette was then tightly closed and moved around and a little up and down for a minute or so, in order to thoroughly mix the two liquids. The cork was again inserted in the tube and the whole left undisturbed for just half an hour. At the expiration of that time another weighed dish of mercury was substituted for the last one and left there for another half-hour, when the mercury vessel, as well as the tube and pipette, were removed. The amount of mercury moved during this last half-hour should, if the thermal equilibrium disturbed by the heat evolved or absorbed by the mixing of the liquids has reëstablished itself, and if there has supervened no change in the velocity of the movement of the mercury, be equal to the amount moved in the half-hour before the introduction of the liquids, and in the half-hour elapsing just before they are mixed. This was generally the case, the deviation always being very slight, and the average of these amounts was taken as the true correction to be applied.

All weighings were made with great care, since an error of one milligram entails an error of several hundredths of a heat unit. It is believed that the results of the experiments are accurate to within less than one-half of a calorie.

The calorimetric unit employed is defined by the amount of heat

required to melt a volume of ice equal to that occupied by 0.01544 gram of mercury at 0°.

The liquids used as material for the investigation had all been carefully purified; in foot-notes are indicated the methods of purification and their boiling-points (uncorr.).

Experimental Results.

When a pair of liquids was taken for the determination of the heat effect of mixing them, about equal quantities of each were weighed out for the first estimation. If the thermal effect proved to be less than that capable of detection by the apparatus, commonly no other mixtures were examined, it having been found that the maximum heat effect was produced when the amounts of the liquids mixed were about the same. An evolution or absorption of heat might nevertheless have been found if other proportions had been investigated, although this is not very probable. Such mixtures as did not appear to exhibit any heat effect are given first. The minus sign before a number indicates an absorption of heat; the positive sign, an evolution of heat.

TABLE I.

HEAT EFFECT OF MIXING MONOCHLORBENZENE[1] AND TOLUENE.[2]

	I.	II.
Chlorbenzene	3.0028 g.	3.7715 g.
Toluene	4.3032	4.2190
Calorimeter correction in weight of mercury	−0.0013	−0.0014
Weight of mercury moved	−0.0018	−0.0020
Weight of mercury moved due to mixing liquids	−0.0005	−0.0006
Heat effect in calories	−0.032	−0.033

[1] Commercial, chemically pure monochlorbenzene was distilled in fractions until nearly half of it boiled at 131°.8 to 131°.9, under a pressure of 757 mm. of mercury.

[2] The toluene had been fractionally distilled until more than a pound of it boiled constantly at 110°.1, under a pressure of 758 mm. of mercury.

TABLE II.

HEAT EFFECT OF MIXING MONOBROMBENZENE[1] AND TOLUENE.[2]

	I.	II.
Brombenzene	4.9530 g.	1.1611 g.
Toluene	4.3680	7.3887
Calorimeter correction in weight of mercury	−0.0009	−0.0010
Weight of mercury moved	−0.0020	−0.0005
Weight of mercury moved due to mixing liquids	−0.0011	+0.0005
Heat effect in calories	−0.072	+0.032

TABLE III.

HEAT EFFECT OF MIXING ETHYL ETHER[3] AND TOLUENE.[2]

Ether	6.9858	grams.
Toluene	3.7256	"
Calorimeter correction in weight of mercury	−0.0033	"
Weight of mercury moved	−0.0033	"
Weight of mercury moved due to mixing liquids	0.0000	"
Heat effect in calories	0.000	

TABLE IV.

HEAT EFFECT OF MIXING ETHYL IODIDE[4] AND TOLUENE.[2]

Ethyl iodide	7.8668	grams.
Toluene	6.1445	"
Calorimeter correction in weight of mercury	−0.0130	"
Weight of mercury moved	−0.0129	"
Weight of mercury moved due to mixing liquids	+0.0001	"
Heat effect in calories	+0.006	

Since the freezing-point of benzene is higher than that of water, it was impossible to employ it in the ice calorimeter in the pure state; accordingly a mixture containing 97.37 per cent of the

[1] Of about a pound fractionally distilled, nearly 150 grams were obtained, boiling at 154°.3 to 154°.5, under a pressure of 761 mm. of mercury.

[2] The toluene had been fractionally distilled, until more than a pound of it boiled constantly at 110°.1, under a pressure of 758 mm. of mercury.

[3] The ethyl ether had been washed repeatedly with water, dried over fused calcium chloride, and finally distilled from phosphoric anhydride. Almost the whole of it boiled at a constant temperature.

[4] Rectified over phosphoric anhydride, the ethyl iodide boiled at 72°.5, under a pressure of 757 mm. of mercury.

hydrocarbon and 2.63 per cent of monochlorbenzene was prepared, and it was with this mixture that the determination recorded in Table V. was made.

TABLE V.

HEAT EFFECT OF MIXING CHLORBENZENE[1] AND BENZENE.[2]

Mixture benzene and chlorbenzene	3.0208	grams.
Chlorbenzene	6.3470	"
Calorimeter correction in weight of mercury .	−0.0013	"
Weight of mercury moved	−0.0030	"
Weight of mercury moved due to mixing liquids	−0.0017	"
Heat effect in calories	−0.101	

The rest of the mixtures examined showed so appreciable thermal effects that several proportions of the liquids were mixed, and in the following tables are recorded the results. In order to obtain a uniform means of comparison, the quantities of liquids mixed are calculated in molecular per cents, and the amounts of heat increased so as to correspond to these masses. In this way, the numbers representing the amounts of heat change when certain numbers of gram-molecules are mixed, come out over a hundred times greater than those actually determined. Accordingly, it must be borne in mind that the units and tens of the numbers communicated have hardly any significance.

TABLE VI.

HEAT EFFECT OF MIXING ETHYL IODIDE[3] AND ETHYL ETHER.[4]

Grams C_2H_5.	Grams $C_4H_{10}O$.	Per cent C_2H_5I.	Molec. per cent C_2H_5.	Mercury moved.	Calorimeter correction.	Calories.	Cal. per mols.
2.4240	9.3465	20.595	10.955	−0.0110	0.0000	−0.71	− 632
8.3683	5.9185	58.573	40.146	−0.0053	+0.0125	−1.18	− 863
13.8745	5.2520	72.543	55.616	−0.0300	0.0000	−1.92	−1215

[1] Commercial, chemically pure monochlorbenzene was distilled in fractions until nearly half of it boiled at 131°.8 to 131°.9, under a pressure of 757 mm. of mercury.

[2] Commercially pure benzene was treated with sulphuric acid to remove thiophene, fractionally crystallized to constant melting-point, viz. 5°.42, and distilled over sodium. Boiling-point was 80°.1, under a pressure of 757 mm. of mercury.

[3] Rectified over phosphoric anhydride, the ethyl iodide boiled at 72°.5, under a pressure of 757 mm. of mercury.

[4] The ethyl ether had been washed repeatedly with water, dried over fused calcium chloride, and finally distilled from phosphoric anhydride. Almost the whole of it boiled at a constant temperature.

TABLE VII.

HEAT EFFECT OF MIXING CARBON BISULPHIDE[1] AND TOLUENE.[2]

Grams C_7H_8.	Grams CS_2.	Per cent C_7H_8.	Molec. per cent C_7H_8.	Mercury moved.	Calorimeter correction.	Calories.	Cal. per mols.
1.6035	13.2050	10.829	9.117	−0.0420	+0.0080	−3.22	−1695
3.6267	12.4130	22.610	19.443	−0.0871	+0.0061	−6.00	−2971
6.8225	7.0721	49.101	44.350	−0.1105	+0.0095	−7.81	−4648
10.6800	1.8372	85.322	82.766	−0.0605	−0.0020	−3.80	−2701
10.5282	0.5040	95.518	94.517	−0.0050	+0.0065	−0.76	− 615

TABLE VIII.

HEAT EFFECT OF MIXING CHLOROFORM[3] AND TOLUENE.[2]

Grams C_7H_8.	Grams $CHCl_3$.	Per cent C_7H_8.	Molec. per cent C_7H_8.	Mercury moved.	Calorimeter correction.	Calories.	Cal. per mols.
0.6075	6.8166	8.182	10.375	+0.0708	−0.0010	+ 4.53	+ 7,101
2.8565	6.1682	31.562	37.560	+0.1962	−0.0038	+12.91	+15,669
2.1741	3.1679	40.698	47.120	+0.1215	−0.0072	+ 8.33	+16,493
6.0145	2.0438	74.637	79.264	+0.1108	−0.0038	+ 7.40	+ 8,996
7.0400	0.6445	91.619	93.406	+0.0110	−0.0030	+ 0.50	+ 636

TABLE IX.

HEAT EFFECT OF MIXING CARBON TETRACHLORIDE[4] AND TOLUENE.[2]

Grams C_7H_8.	Grams CCl_4.	Per cent C_7H_8.	Molec. per cent CCl_4.	Mercury moved.	Calorimeter correction.	Calories.	Cal. per mols.
0.4200	7.2987	5.441	8.785	−0.0080	−0.0042	−0.25	− 474
1.3662	6.9568	16.415	24.735	+0.0005	−0.0057	−0.41	− 666
3.7530	6.5552	36.408	48.937	+0.0050	−0.0114	+1.13	+1272
5.1212	4.2560	54.613	71.717	+0.0162	−0.0066	+1.51	+1504
6.0023	1.8523	76.418	84.434	+0.0070	−0.0066	+0.88	+1139
6.3920	0.8978	87.684	93.320	−0.0102	−0.0042	−0.32	− 419

[1] The carbon bisulphide was dried over phosphoric anhydride and distilled over mercury; it boiled constantly at 46°.25, under a pressure of 756 mm. of mercury.

[2] The toluene had been fractionally distilled until more than a pound of it boiled constantly at 110°.1, under a pressure of 758 mm. of mercury.

[3] The chloroform had been fractionated to constant boiling-point, and was finally distilled over phosphoric anhydride; its boiling-point was 61°.3, under a pressure of 759 mm. of mercury.

[4] The sample had been fractionally distilled over phosphoric anhydride, and boiled at 76°.7, under a pressure of 754 mm. of mercury.

TABLE X.

HEAT EFFECT OF MIXING CARBON TETRACHLORIDE[1] AND CHLOROFORM.[2]

Grams CCl_4.	Grams $CHCl_3$.	Per cent CCl_4.	Molec. per cent $CHCl_3$	Mercury moved.	Calorimeter correction.	Calories.	Cal. per mols.
0.7632	11.9765	5.986	4.713	−0.0210	−0.0151	−0.45	− 369
1.3275	6.2995	16.649	14.053	−0.0302	−0.0190	−0.71	−1193
8.9100	5.2060	63.120	57.046	−0.0892	−0.0052	−5.42	−5353
12.5720	2.6480	82.599	78.643	−0.0750	−0.0213	−3.41	−3289
11.8203	1.6395	87.820	84.838	−0.0580	−0.0180	−2.59	−2786
11.3480	0.3600	97.199	96.072	−0.0364	−0.0152	−1.40	−1799

Discussion of Results.

In a paper "On the Vapor Tensions of Mixtures of Volatile Liquids,"[3] I have had occasion to discuss the mixing of liquids without the production of any appreciable thermal effect, in connection with considerations on their vapor tensions, and in this present paper more experimental data are given in corroboration of the views stated in that place. It may be added here, to what was said there, that it is not probable that absolutely *no* heat change occurs when certain liquids are mixed. The amount of heat evolved or absorbed is, however, so slight that it escapes detection; with more delicate instruments, no doubt, its amount could be ascertained.

In regard to whether heat will be evolved or absorbed in appreciable measure, there seems to be no criterion. Thus, it seems probable, if two liquids A and B each mix with another liquid C, without a measurable heat effect, that these two liquids will mix with one another without giving rise to any evolution or absorption of heat. This is, however, not the case, for both ethyl ether and ethyl iodide mix with toluene without a thermal change (Tables III. and IV.), and yet, when mixed with each other, give a not inconsiderable heat effect (Table VI.). A curious result is ob-

[1] The chloroform had been fractionated to constant boiling-point, and was finally distilled over phosphoric anhydride; its boiling-point was 61°.3, under a pressure of 759 mm. of mercury.

[2] The sample had been fractionally distilled over phosphoric anhydride, and boiled at 76°.7, under a pressure of 754 mm. of mercury.

[3] Journal of the American Chemical Society, Vol. XVII., August, 1895.

tained with mixtures of chloroform, carbon tetrachloride, and toluene. When carbon tetrachloride and chloroform are mixed, heat is absorbed, and, indeed, the heat absorption reaches a maximum when about equal quantities of each liquid are mixed. The mixing of chloroform and toluene gives, on the other hand, an evolution of heat, attaining its maximum when about the same number of molecules of each liquid is taken. With mixtures of carbon tetrachloride and toluene, an entirely different behavior is found. If a small proportion of either of the liquids be added to the other, heat is absorbed; when, however, the proportions in which the liquids are mixed become more nearly equal, an evolution of heat is observed. This difference of behavior in the three liquids is enigmatical. Chloroform and carbon tetrachloride being so similar, both chemically and physically, it might be expected that they would behave more similarly, as regards their thermal effects, when mixed with toluene, a liquid which had shown itself to give very simple results when mixed with ether, ethyl iodide, etc. Our knowledge of the subject does not at present permit us to get at the secret of the affair.

When carbon bisulphide and toluene are mixed, heat is absorbed, no matter what the relative proportions of the two liquids, and the amount of heat is greater than that absorbed in the mixing of ethyl iodide and ether. This greater absorption of heat, occasioned by the mixing of the first two liquids, may be due to the fact that carbon bisulphide is slightly associated; and it is probable that heat is required to break up the associated molecules.

Influence of Temperature upon the Heat Effect of Mixing Normal Liquids.

It is of some interest to consider what influence a change of temperature exercises upon the amount of heat absorbed or evolved when liquids are mixed. It may be that the absolute amount of heat brought into play is different at various temperatures, and in some cases the mixing of liquids will occasion an evolution of heat at one temperature, and an absorption of heat at another. Certain energetical considerations will afford us a relation between the heat effects of mixing liquids at different temperatures and the

specific heats of the mixed and unmixed liquids, and by its aid and comparison with experimental data on the specific heats of mixtures of liquids, we will obtain a definite answer to our question.

Let two liquids A and B be mixed at the temperature T_1, whereby a positive or a negative heat effect amounting to $\pm Q$ is occasioned; for the sake of simplicity, we will assume the heat effect to be positive, as such a supposition is in nowise a restriction to the generality of the results. The mixture is now heated to the temperature T_2, in which operation an amount of heat equal to $(T_2-T_1)c_1$ is needed, c_1 representing the specific heat of the mixture in the temperature interval (T_2-T_1). At the temperature T_2 the two liquids are separated, the act of separation being accompanied by an absorption of heat amounting to Q_2. The separated liquids are now cooled down to the original temperature, when $(T_2-T_1)c_2$ units of heat are given out, if c_2 represents the sum of the heat capacities of the liquids. As the cycle of operations is now completed, we may, in accordance with the law of the conservation of energy, form the following equation:

$$Q_1+(T_2-T_1)c_2=Q_2+(T_2-T_1)c_1,$$

or (1)
$$C_2-C_1=\frac{Q_2-Q_1}{T_2-T_1}.$$

Accordingly the difference between the specific heats of the pure liquids and their specific heats when mixed is equal to the increase of the heat effect of mixing them per degree of rise of temperature.

Now it results from the experiments of J. H. Schüller,[1] of W. Alexejew,[2] and of F. L. Perrot,[3] that the difference between the specific heats of mixed and unmixed normal liquids is less than that due to unavoidable experimental errors; a normal liquid preserves its specific heat in mixture. From this experimental fact it follows that the first member of equation (1) is equal to zero in the case of mixtures of normal liquids, and hence the second member is equal to zero also. A change of temperature, then, has no appreciable influence upon the thermal effect of mixing normal liquids.

CHICAGO, January 24, 1896.

[1] Pogg. Ann. Ergänzungsband, V., p. 210, 1871.
[2] Wiedemann's Annalen, 28, p. 322, 1886.
[3] Arch. des sciences physiques et naturelles, 32, pp. 145, 254, and 337, 1894.

THE INFLUENCE OF HEAT, OF THE ELECTRIC CURRENT, AND OF MAGNETIZATION UPON YOUNG'S MODULUS.

BY MARY CHILTON NOYES.

IN the PHYSICAL REVIEW for January–February, 1895,[1] an article was published describing a series of experiments which had been made in the physical laboratory of Cornell University, to determine the effect of temperature upon Young's modulus for a piano wire. An electric current was used as the source of heat, and a series of different temperatures employed. The experiments showed very clearly that Young's modulus for a piano wire decreases as the temperature is raised from 15° to 180° C., and that the decrease is nearly, if not exactly, proportional to the increase in temperature. The value of the thermal coefficient was likewise determined.

There were, however, other questions which were raised rather than settled by the experiments. When the wire was heated by an electric current through a helix surrounding it, the results were quite regular; but when the current was sent through the piano wire itself, results were obtained which were so irregular that no certain conclusions could be drawn from them. Some of them seemed to indicate that the current through the wire had a very perceptible effect upon the elasticity; others made it doubtful whether there was any effect aside from that due to the heat. It seemed desirable to conduct a series of experiments by the same general method, but so planned as to distinguish between the effects due to the heat, to the longitudinal magnetization, and to the electric current through the wire. For this purpose apparatus similar in all essential particulars to that used at Cornell, and described in the previous article, was arranged in the physical laboratory of Western Reserve University. A solid block of oak

[1] PHYSICAL REVIEW, Vol. II., No. 10, p. 277.

of sufficient length was placed upon a stone pier which was isolated from the floor so as to avoid jars from other parts of the building. The wire was passed through a glass tube, attached to a support at one end, and passed over an Atwood wheel at the other. Every precaution was taken to avoid drafts of air or anything which would cause variation of temperature. A large cloth screen was placed between the apparatus and the hot-air register; the Atwood wheel was carefully covered with a cloth, and the wire at the other end was protected in a similar way.

When the wire was heated by a current through the helix around the tube, the temperature was determined by three thermometers placed inside the tube, but so arranged as not to touch it. Before using the thermometers, a table of corrections was made for them. To do this they were compared with a standard thermometer between 0° and 100°; the freezing and boiling points were determined; and the stems between 100° and 200° were calibrated by using a thread of mercury and comparing with the parts between 0° and 100°. The corrections so determined were applied to all the readings taken. When the wires were heated by a current through them, the temperatures were determined by the elongation, the coefficient of linear expansion being previously determined by noticing the elongation when the wires were heated by the current around them. Sometimes the highest temperature used in a series of observations was determined both by noticing the elongation when the wire was heated and the subsequent contraction after the current had stopped; the results usually agreed within a fraction of a degree. Some experimenters have found that an electric current through a wire produces a greater elongation than would be caused by the same temperature produced in some other way. The difference is, however, so small that it has not seemed necessary to take it into account in determining the temperatures.

The micrometer heads of the microscopes had fifty divisions; in all the readings half-divisions were used. It was found that 4080 half-divisions were equal to one millimeter. The diameters of the wires were measured by two or three micrometer wire gauges and the average results taken.

The wires were stretched by a weight equal to about one-half the breaking weight for twenty-four hours or longer before the first observations were made, and the maximum weight used in the determinations was a little less than the stretching weight. With the piano wires, the same weights were always used for the same kind of wire, so that the results obtained in the different experiments might be comparable. In determining the modulus, all the weight added was put on at once instead of using intermediate weights, as had been done in most of the previous work. The additional weight was always put on and taken off before the first reading was taken, and the readings were made as soon as possible after placing the weights. Usually the weight was put on and removed three times for one determination, so that the result was the average of six values; in many cases a larger number of observations was taken. The attempt was made to secure so steady a temperature that the readings before placing the weights and after removing them would not vary more than one or two half-divisions, but it was not always found possible to obtain this condition. If the variations were a little more, but all in the same direction and of the same amount, showing that the change in temperature was regular, it was thought that the average result could not be far wrong. The matter was tested by comparing the average result when there was a considerable, but regular, change in the readings with that obtained a little later with the same current but after the temperature had become steady; the results usually differed only about one-tenth of one per cent.

The wires were measured to one one-hundredth of a millimeter with a standard meter rule. In computing the moduli, this length was corrected for the elongation corresponding to each temperature employed.

With the first wire used, the elongation for one degree was found to be 0.01137 mm.; the length of the wire was 952.00 mm., making the coefficient of expansion 0.000012. The same coefficient was used in determining the change in the cross-section with change of temperature, and this correction was also used in making the calculations.

Experiment 1.

A piece of number six piano wire was used in this series of observations. It was heated alternately by the magnetizing current and by the current through the wire itself. The lowest weight used was 3.5 Kg., and the additional weight used to produce the elongation was 1.0 Kg. A number of observations made before the adjustments were sufficiently perfect to give concordant results were discarded.

Observations were first made with current through the magnetizing helix, then with current in the wire itself. The set with the current through the wire are somewhat irregular, but with a single exception are higher than those that had been previously obtained with the magnetizing helix. When the magnetizing current was again used, the values found fall between those of the first and second sets. A final set, with the current again through the wire, are more regular than the first set obtained in the same way, and are on the whole higher than any of the preceding sets.

The results show an increase from heating the wire alternately by the two methods; but there is little to indicate whether the effect is due to the heat alone, to the current, or to the magnetization.

In order to see if a continuation of the current would change the modulus, a number of determinations were made with an interval between the sets of observations, but making no change in the conditions. The results differed no more than the probable errors of observation.

Experiment 2.

Another piece of the same kind of wire as had been used in the previous experiment was adjusted and heated in a similar way, only the current through the wire was used first, and afterwards the magnetizing current. The following table gives the numerical results obtained, and (Fig. 1) represents them graphically.

TABLE I.

Current left to right, through wire.

No.	Date.	Temperature.	Elon. for 1 Kg.	No. of obs.	Modulus.
1	March 14	23°.5	1442.44	7	21,234
2	" 15	24°.9	1140.50	6	21,268
3	" 15	27°.2	1145.50	6	21,173
4	" 15	34°.1	1145.05	4	21,179
5	" 15	43°.2	1150.63	6	21,075
6	" 15	50°.3	1157.63	8	20,947
7	" 15	63°.6	1160.23	6	20,896
8	" 15	83°.0	1172.28	6	20,676
9	" 15	97°.9	1189.90	6	20,366
10	" 16	33°.8	1146.56	12	21,152
11	" 16	45°.8	1148.33	8	21,118
12	" 16	64°.9	1155.00	4	20,992
13	" 16	91°.4	1172.27	6	20,675
14	" 16	112°.7	1186.85	8	20,416
15	" 16	137°.1	1200.87	3	20,171
	Current right to left, through wire.				
16	March 18	27°.2	1131.98	5	21,426
17	" 18	76°.7	1158.67	12	20,920
18	" 18	93°.1	1172.36	8	20,672
19	" 18	116°.0	1191.90	4	20,328
20	" 18	157°.8	1209.15	4	20,028
21	" 18	183°.5	1231.42	10	19,654
22	" 19	77°.1	1155.40	4	20,979 (?)
23	" 19	95°.0	1176.47	6	20,599
24	" 19	111°.6	1182.01	8	20,300
25	" 19	123°.8	1186.58	10	20,418
26	" 19	150°.3	1198.60	8	20,207
27	" 19	166°.6	1209.78	8	20,014
28	" 20	13°.3	1134.07	6	21,394
	Current right to left, through magnetizing helix.				
29	March 20	28°.8	1134.78	8	21,373
30	" 20	37°.4	1140.03	7	21,272
31	" 20	42°.7	1140.50	8	21,262
32	" 20	50°.4	1142.59	10	21,223
33	" 21	33°.5	1134.66	8	21,374
34	" 21	51°.0	1139.20	8	21,286
35	" 21	68°.1	1153.45	4	21,018
36	" 21	85°.3	1157.50	3	20,939

TABLE I. (*continued*).

No.	Date.	Temperature.	Elon. for 1 kg.	No. of Obs.	Modulus.
	Current left to right, through magnetizing helix.				
37	March 22	39°.1	1137.76	8	21,315
38	" 22	61°.5	1148.98	5	21,102
39	" 22	86°.9	1154.60	6	20,993
40	" 22	90°.3	1165.00	4	20,804
41	" 22	105°.1	1169.03	6	20,728
42	" 23	15°.6	1128.84	7	21,498
	Current left to right, through wire.				
43	March 23	39°.9	1133.37	6	21,398
44	" 23	58°.2	1137.53	4	21,315
45	" 23	90°.5	1159.90	4	20,895
46	" 25	77°.3	1147.70	8	21,120
47	" 25	93°.4	1157.28	5	20,942
48	" 25	150°.0	1199.63	6	20,188
49	" 26	19°.8	1129.27	6	21,481
50	" 26	34°.2	1138.87	6	21,295
51	" 26	42°.5	1147.29	7	21,136
52	" 26	51°.2	1139.35	4	21,282
53	" 26	76°.2	1146.63	6	21,141
54	" 26	92°.5	1155.68	8	20,971
55	" 26	113°.9	1172.90	8	20,657
56	" 26	150°.0	1202.32	10	20,143

$L = 954$ mm. at 18°. $Q = 0.16046$ sq. mm. at 18°. $P = 1$ Kg.

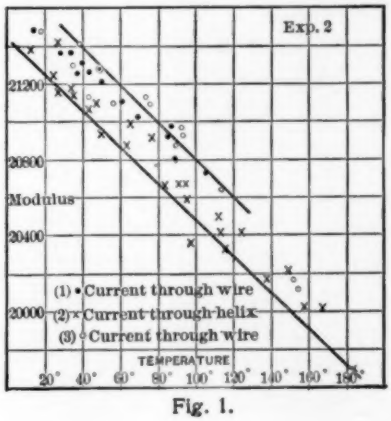


Fig. 1.

The values found for the first set of observations show a gradual increase in the modulus as the heating is repeated; some of the later values fall very nearly in the same line as those of the next set, which were obtained with the magnetizing current. Most of the final set, when the current was again sent through the wire, are higher than either of the preceding sets. There is the same progressive increase in elasticity with the alternate methods of heating that had been found in the preceding experiment.

Experiment 3.

A third piece of the number six piano wire was taken, and the same order used in the methods of heating as in the first experiment.

After a few readings had been obtained, it was discovered that the cloth used to protect the Atwood wheel from drafts of air touched the wire, making the results uncertain; hence the values for the first heating were rejected. The subsequent results were more regular than in either of the previous experiments, and the results obtained in the third and fourth sets fall almost exactly in the same line, which seems to indicate that the wire had reached a condition such that its elasticity would not have been much modified by further repetition of the heating or of the magnetization.

The three experiments all show that the elasticity of a piano wire is increased by heating it alternately by a magnetizing current and by a current through the wire itself. The fact that the order in which the two methods are used makes no essential difference in the result, makes it probable that the effect is due to the heat alone.

In this, as in several of the other experiments, both the magnetizing current and the current through the wire were reversed a number of times; no difference in the effect of the current could be detected. This fact furnishes additional evidence that neither the longitudinal nor the circular magnetization is the cause of the change in the elasticity.

Experiment 4.

A larger piano wire was used for this experiment in order to make it more certain that the results obtained did not depend upon any peculiarity in the particular specimen of wire employed. The results obtained are much the same as those that had been found with the smaller wire, but the increase in elasticity from the heating is less than in the other cases, and a condition in which a repetition of either form of heating produced no further change was sooner reached.

Experiment 5.

In order to determine with greater certainty whether heat alone was the cause of the increase in the modulus produced by alternating the two methods of heating, a double coil was so arranged that the current flowed through one part in one direction and the other part in the opposite direction, thus making it non-inductive. This coil was used for heating another piece of the number six wire. Figure 2 shows the results obtained by this method. There is the same kind of increase in elasticity with each alternation of the method of heating that had been found when using the magnetizing helix. The conclusion seems inevitable that the longitudinal magnetization at least has no appreciable effect upon the result.

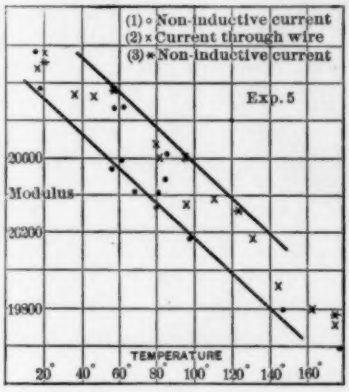


Fig. 2.

Experiment 6.

The results of each of the previous experiments showed a change in the modulus produced by repeated heating. It therefore seemed desirable to compare the moduli obtained with the different methods of heating applied to a wire that had already been heated and cooled so many times that further repetition of the treatment would produce no change in the elasticity. For

this purpose a piece of the number six piano wire was placed in the tube inside the magnetizing helix, and was repeatedly heated by a current through the helix.

Some of the results obtained in the previous year indicated the possibility that repeated magnetization might modify the effects produced in a wire by a current through it. The plan of this experiment made it possible to test this point also.

After heating and magnetizing the wire a number of times, a series of values for the modulus was found when it was heated by the magnetizing current, and the following day a corresponding series when it was heated by a current through the wire itself. The results are plotted in Fig. 3. They all fall very close to a straight line, with no appreciable difference in the results obtained by the two methods of heating. These results show that if there is any difference in the effects produced upon the elasticity of a piano wire by magnetizing it longitudinally and circularly, that difference is too small to be detected with any certainty by this method of experiment.

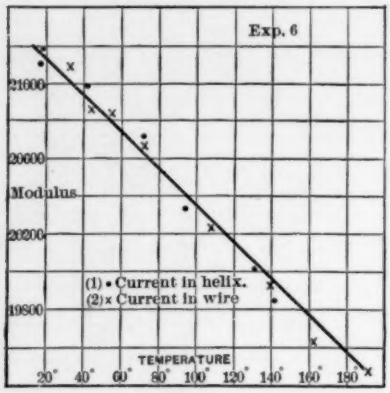


Fig. 3.

Since the results of the fifth experiment, compared with those of the first three experiments, showed that the heating effects produced by a non-inductive current and by a magnetizing current are the same, the proof seems conclusive that neither longitudinal magnetization nor a current through a wire produce any appreciable effect upon Young's modulus aside from that which is due to the accompanying heat.

From the results obtained in the first three experiments, it was computed that the permanent increase in elasticity due to repeated heating is about 1.45 per cent of the value found for the modulus by producing the line passing through the first set of results until it intersects the zero line. The corresponding change found in

the fifth experiment is 1.90 per cent of the value at 0°; the greater increase may be due to the fact that higher temperatures were secured in this case with the current around the wire than had been used in the earlier experiments; the cooling took place much more slowly after stopping the current through the helix than when the current was through the wire itself; this more gradual cooling might easily account for the larger increase in elasticity.

The thermal coefficient was determined in connection with the different experiments by drawing lines which would correspond to the average decrease of the modulus with the increase of temperature, and comparing that decrease with the zero value corresponding to the final set of results. The average value found in this way from experiments 1, 2, 3, and 5, is 4.65 per cent for 100°. The value found in a similar way from the results of the sixth experiment is 4.55 per cent. This result is more probable than any of the others, since it is difficult to draw a line satisfactorily through the results obtained before the wires had been heated sufficiently to reach a permanent condition. Giving equal weight to the average of the four results and to the result of the sixth experiment, we get a value of 4.60 per cent for the thermal coefficient. This is a little smaller than the value found in the previous investigation already cited for the larger wire experimented with, but is just the same as that found for the smaller wire.

A few results which were obtained with this wire at temperatures ranging from 300° to 600°, showed a continued decrease in the modulus with the increasing temperature. The decrease was apparently at about the same rate as that found between 15° and 180°; but these high temperatures could not be determined with sufficient accuracy to be sure that the thermal coefficient remains constant.

Experiment 7.

A piece of the number six piano wire was annealed by heating it inside a glass tube, through which a current of coal gas was passing so as to prevent oxidation. The modulus of the wire was

then determined when it was heated by the non-inductive current and by a current through the wire. Another piece of the same kind of wire was heated while covered with powdered charcoal, to prevent oxidation. The modulus was then determined when it was heated by the non-magnetizing current, by a current through the wire, and by a magnetizing current. The results, which were entirely analogous to those of the previous experiments, make it safe to conclude that with an annealed wire, as with the unannealed, there is no appreciable effect except that due to heat. The thermal coefficient is smaller for the annealed than for the unannealed wire, being only 3.4 per cent for 100°.

Experiment 8.

A piece of silver wire 0.48 mm. in diameter was used for this experiment. Young's modulus was determined when the wire was heated by a current through the non-inductive coil, and when it was heated by a current through the wire itself. Figure 4 shows the results. The observations are numbered so that the progressive change in the modulus may be traced more clearly. Comparing numbers 1, 4, and 7, we see an increase in the modulus each time the wire was heated. The still greater change between numbers 7 and 16 was probably due to the fact that in determining number 15 the wire was stretched beyond its elastic limit. All of the results from the sixteenth through the twenty-fourth are close to the same line. Between numbers 21 and 22 there was an interval of about a month during which the wire had remained unstretched; a comparison of results obtained before and after that time shows no appreciable change in the elasticity.

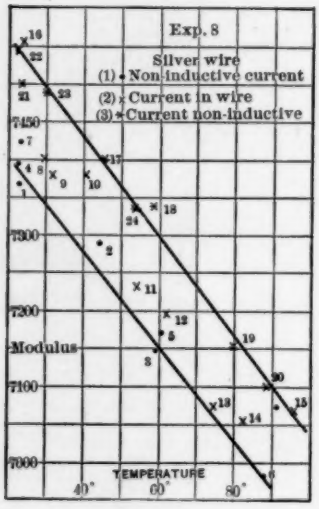


Fig. 4.

Number 15, and some of the other results obtained at the higher temperatures, are somewhat uncertain. No appreciable change in

the elastic limit with the increase in temperature had been anticipated, and the weights chosen were those found suitable at the temperature of the room. It was found, however, that at about 80° the larger weight that had been used at the lower temperature, 2.9 Kg., slightly exceeded the elastic limit; and at 88° the heaviest weight that could be used was 2 Kg. These facts led to an investigation of the change in the elastic limit with change of temperature. The results obtained are shown in Fig. 5. Numbers 1 to 5 were obtained one day, and numbers 6 to 12 two or three days later, while number 13 was twenty-four hours after number 12. There was not time to contrive any very accurate method of determining the elastic limit that could be employed with the apparatus in use, and the results are not as definite as could be desired. They seem, however, to show plainly that the elastic limit decreases with increasing temperature, and also that between 20° and 115° the decrease is nearly, if not exactly, proportional to the increase in temperature. They also show a decrease in the elastic limit with the repeated heating and stretching.

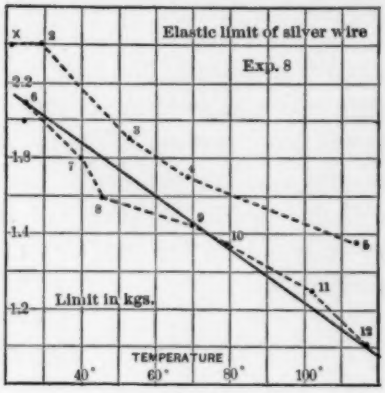


Fig. 5.

Determinations of the modulus made after numbers 5 and 13 in the elastic-limit series, gave the values 7605 at 23°, and 7954 at 25°. These values, and also number 16, previously referred to, show a permanent increase in the elasticity produced by stretching the wire beyond the elastic limit while that limit was temporarily lowered by heating.

Experiment 9.

A piece of copper magnet-wire 0.64 mm. in diameter was heated by the same methods that had been employed with the silver wire. The results were somewhat affected by the application of unsuita-

ble weights, but they sufficed for the computation of the thermal coefficient of the modulus.

It was found to be 13.3 per cent for 100°; whence

$$M_t = M_0(1 - 0.00133\,t).$$

The elastic limit was also determined at three temperatures. The results show a decrease which is proportional to the increase in temperature. (See Table III.)

The coefficient of linear expansion of the wire was determined when it was heated by using the non-inductive coil, and this coefficient was employed in determining the temperatures when heating by the other method. The coefficient found was 0.0000153. This is smaller than the coefficient usually given; the low value is probably due to the quality of the copper wire tested. The small value found for the modulus may perhaps be accounted for in a similar way.

Experiment 10.

A smaller piece of copper magnet-wire was used for this experiment. Its diameter was 0.50 mm. The following table gives the

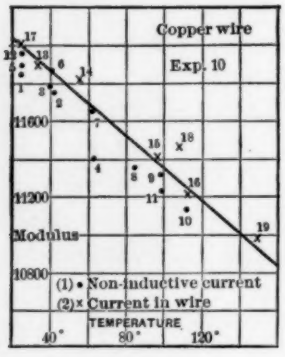


Fig. 6.

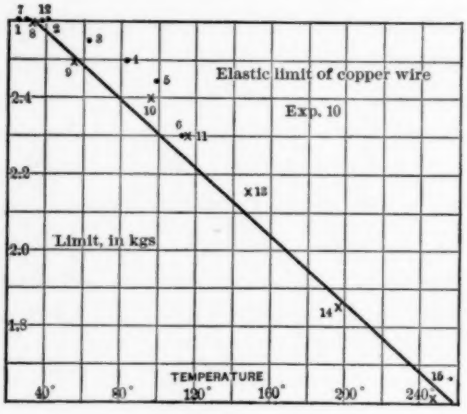


Fig. 7.

results that were obtained, and Figs. 6 and 7 represent them graphically.

TABLE II.

Non-inductive Current.

No.	Date.	Temperature.	Elon. for 0.6 Kg.	No. of obs.	Modulus.	Elastic limit.	No. (Elastic limit series).
1	June 14	25°.5	983.60	6	11,841		
2	" 14	40°.8	990.73	6	11,754		
3	" 14	40°.2	988.56	10	11,780		
4	" 14	62°.8	1020.87	3	11,402		
5	" 15	24°.7	979.80	4	11,887	2.60 Kg.	1
6	" 15	40°.3	981.37	7	11,866	2.60	2
7	" 15	62°.9	998.84	7	11,653	2.55	3
8	" 15	82°.8	1025.80	4	11,345	2.50	4
9	" 15	97°.9	1027.29	7	11,327	2.45	5
10	" 15	111°.6	1045.30	4	11,129	2.30	6
11	" 15	98°.8	1036.30	6	11,228		
			Current through wire.				
12	June 17	25°.1	973.93	6	11,959	2.6	7
13	" 17	33°.3	978.50	4	11,901	2.6	8
14	" 17	55°.0	984.30	6	11,827	2.5	9
15	" 17	96°.0	1019.76	5	11,409	2.4	10
16	" 17	112°.9	1036.77	6	11,218	2.3	11
17	" 17	25°.0	972.05	4	11,982	2.6	12
18	" 18	107°.0	1014.60	6	11,465		
19	" 18	149°.3	1057.33	6	10,994	2.15	13
20	" 18	188°.3	1146.63	6	10,132	1.85	14
21	" 18	248°.8	1050.09	9	9,209	1.60	15

$Q = 0.1998$ sq. mm. $L = 950.91$ at 25°.5. $P = 0.6$ Kg.

If we notice numbers 1, 5, 12, and 17, all of which were obtained at the temperature of the room, we see an increase in the elasticity after each time that the wire was heated, although the change from 12 to 17 was very slight. The increase may have been partly due to stretching the wire in determining the elastic limit, and not wholly to the heat; the irregularity of the values after the seventeenth is probably due to the same cause.

The results found for the elastic limit show a decrease which is very nearly proportional to the increase in temperature. As was

found to be true with the silver wire, the elastic limit decreased slightly with repeated heating and stretching, while the elasticity was increased by the same treatment.

The following table gives a comparison of the results obtained with the copper wires tested in this and the preceding experiment:

TABLE III.

	1	2
Coefficient of Expansion	0.0000153	0.0000164
Thermal coefficient of elasticity	0.00133	0.000698
Modulus at 25°	10020	11980
Thermal coefficient of elastic limit . . .	0.0034	0.00165

As the table shows, the differences in all of the properties tested are very marked. The thermal coefficient of elasticity, and also of the elastic limit, are nearly twice as large in the first case as in the second. Such results serve rather to call attention to the wide variations in the properties of apparently similar specimens of wire than to fix the values of the coefficients determined.

Conclusion.

The following table gives a summary of results obtained from the experiments described in this article and the one previously published. The results for the piano wires are for temperatures ranging from about 15° to 180°, for the silver wire and the first copper wire the range was from 20° to 80° or 90°:

TABLE IV.

Kind of wire.	Diam.	Per cent of change in modulus for 100°.	Per cent of permanent change in modulus.	Per cent of change in elastic limit for 100°.
Piano wire	0.40 mm.	5.0		
Piano wire	0.26	4.6		
Piano wire	0.45	4.6		
Piano wire	0.49	4.3		
Average for piano wire . .		4.6	1.5	
Annealed piano wire . . .	0.45	3.4	1.27	
Silver wire	0.48	8.2	1.8	69.2
Copper wire	0.64	13.3		33.9
Copper wire	0.50	7.04	1.15	16.8

The results obtained show that neither magnetization nor an electric current through a wire produces any appreciable effect upon the size of Young's modulus aside from that which can be attributed to the accompanying heat. All the wires show a permanent increase in elasticity produced by heating them, the increase being greatest for the silver and least for the copper wire.

The thermal coefficient of elasticity is somewhat smaller for annealed than for unannealed piano wire. The values found for the thermal coefficients of silver and copper wire are much larger than those that have been found by others who have worked upon this subject.[1] Perhaps the weights which my method of experiment made necessary were heavier than those used by other experimenters; the thermal coefficient may be quite different for weights nearly as large as the elastic limit from what it would be with smaller weights.

The temporary effects of heat upon the elastic limit of silver and copper wires are very marked. In some electric circuits for which copper wire is employed, it has been found that the wire stretches much more during the summer than it contracts when the cold weather returns. This is doubtless because the elastic limit is so decreased by the summer heat that the weight of the wire between the points of support stretches it beyond this limit. The fact that copper wires vary so much in the effect of heat upon the elastic limit may need to be considered in selecting wires for telephone circuits or other purposes for which long wires are to be employed.

(These experiments were made under the direction of Professor Frank P. Whitman, and the paper was presented as part of a thesis for the degree of Ph.D.)

[1] N. Katzenelsohn, Beiblätter XII., p. 307, 1888. H. Tomlinson, Pro. Roy. Soc., XL. p. 343, 1886.

A PHOTOGRAPHIC STUDY OF ARC SPECTRA. II.[1]

BY CAROLINE WILLARD BALDWIN.

II.

METALLIC SPECTRA.

CERTAIN metals when introduced into the arc tend to obscure the band spectrum, *e.g.* Na, Li, K, Sr, Ba, Ca; while others, as Zn, Cd, Cu, Ag, give the band spectra with equal or increased brilliancy. In no case was the band spectrum entirely invisible, but it was so much weakened by the alkalies that it is not strange that in their presence the carbon bands were not detected by the bolometric measurements of Professor Snow.

In the ensuing paragraphs the results obtained by photographing the arc when cores of the carbons were filled with various alkalies are briefly described and tables of the lines are given.

Lithium Carbonate.

Lithium gives an almost homogeneous carmine-colored arc. The spectrum has much the same general appearance as the spectra from the outer sheaths of the arc, with the addition of the lithium lines, and at a very short distance from the center of the arc the band spectrum is entirely invisible. However, the bright groups are faintly visible in the photographs taken from the center of the arc.

Lithium does not materially affect the other metallic lines present in the ordinary arc spectrum. The lines which are most brilliant in the outer sheaths of the original arc are, with but few exceptions, the strong lines present when lithium is introduced. The carbon lines 3585.99, 3586.04, and 3590.52 are much fainter than in the yellow of the ordinary arc, and are not visible at

[1] Concluded from the PHYSICAL REVIEW, March–April, 1896.

all when the slit is at a little distance from the center of the image, while a line at 3583 is very sharp in all the photographs. The calcium lines 4299.14, 4302.68, 4318.80, 4425.61, 4435.86, and 4456.81 are stronger than in the yellow of the arc, being nearly as strong as 4307.91; but Ca 4527.17 is fainter in comparison to surrounding lines. Line 4527.17 is in fact hardly visible.

Lithium lines photographed.[1]

λ = 2741.39	λ = 3794.9	λ = 3985.94	λ = 4602.37
3232.77	3838.3	4132.44	4972.11
3670.6	3915.2	4273.44	6103.77
3718.9			

Sodium Nitrate.

When sodium is in the arc the flame is homogeneous and quite dense; the band spectrum is not so faint as when lithium is present, still it is much reduced in brilliancy. All of the calcium lines are strengthened. Calcium seems to have been present as an impurity in a number of the salts used. The *D*-lines were reversed both when the nitrate and chloride were used.

Sodium lines photographed.

λ = 2512.23	λ = 4343.7	λ = 4546.03	λ = 5153.72
2543.85	4390.7	4665.2	5670.40
2593.98	4393.7	4669.4	5675.92
2680.46	4420.2	4748.36	5682.90
2852.91	4423.7	4752.19	5688.26
3302.47	4494.3	4979.30	5890.19
3303.07	4500.0	4983.53	5896.16
4325.7	4542.75	5149.19	

[1] The wave lengths of the metallic lines are taken from Kayser and Runge, Ueber die Spectrum der Elemente, with whose measurements the scale readings agreed quite accurately. These tables are not given to establish wave lengths, but to show which of the lines already catalogued were found in these photographs.

Potassium Chloride.

Potassium easily gives a long arc which is homogeneous and very clear, so as to be hardly visible between the carbons. It is of a less intense color than the arc of sodium or of lithium, and seems to be surrounded by a considerable mass of cooler vapor. The carbons are not at a very high temperature. The band spectrum is absent except very near the positive carbon. The strong metallic lines from the original arc are present. The metallic lines appear much as when sodium and lithium are used.

Potassium lines photographed.

$\lambda = 3217.76$	$\lambda = 4047.36$	$\lambda = 4956.8$	$\lambda = 5112.68$
3446.49	4870.8	4965.5	5782.67
3447.49	4943.1	5084.49	5802.01
4044.29	4952.2		

Calcium Chloride.

When calcium is in the carbons, they are as highly incandescent as carbons which contain no metallic salt. The heat of the arc does not seem to be so much diminished as in the preceding cases. The arc shows a more varied formation. There is a blue-violet center, which is decidedly blue near each carbon. This is surrounded by a dark part, while the outer sheath is of an orange tint. The dark part diminishes as the carbons become heated.

In the spectrum the strength of the bands is less affected than by the other metals yet studied; but their hazy appearance is removed, and the fine lines are more sharp. As soon as we pass into the outer sheath, the bands disappear with the exception of a slight indication of the one which terminates at $\lambda = 3885$. The calcium lines remain exceedingly sharp and brilliant in the outer sheath.

As in the ordinary arc, the calcium lines 4581.66 and 4586.12, also lines of unknown origin near 4603., 4586., and 4581., are clearly seen at the negative carbon only, while lines at 4604. and 4576. are visible only at the positive carbon. Line 4226.91 was strongly reversed.

Calcium lines photographed.

λ = 2398.66	λ = 3630.82	λ = 4318.80	λ = 5189.05
2995.06	3644.45	4355.41	5260.58
2997.42	3653.62	4425.61	5261.93
2999.76	3706.18	4435.13	5262.48
3006.95	3737.08	4335.86	5264.46
3140.91	3933.83	4454.97	5265.79
3150.85	3949.09	4456.08	5270.45
3158.98	3957.23	4456.81	5349.66
3179.45	3968.63	4508.04	5513.07
3181.40	3973.89	4509.89	5582.16
3209.68	4092.93	4512.73	5588.96
3215.15	4095.25	4527.17	5590.30
3225.74	4098.82	4578.82	5594.64
3344.49	4226.91	4581.66	5598.68
3350.22	4240.58	4586.12	5601.51
3361.92	4283.16	4685.40	5603.06
3468.68	4288.51	4833.85	5857.77
3474.98	4299.14	4847.22	6102.99
3487.76	4302.68	4878.34	6122.46
3623.15	4307.91	5041.93	

Strontium Oxide.

With strontium the arc has a pear-shaped purple center, the larger end of which rests on the positive carbon. The central part is bluish at each carbon. The outer sheath is of a brilliant red color, and the line between the two parts is very sharp and bright. The carbons are not very hot. They are, indeed, scarcely more than at a red heat. The effect on the spectrum is similar to that of calcium, and the same arrangement of lines at the positive and negative carbon is emphasized. The band spectrum is about as strong as when calcium is present, but it does not disappear quite so completely as in the outer sheaths of the arc.

The number of strontium lines in the vicinity of the bands tends to obscure their character.

Strontium lines photographed.

λ = 2931.98	λ = 3547.92	λ = 4319.39	λ = 4784.43	λ = 5156.37
3199.1	3628.62	4326.60	4812.01	5222.43
3200.4	3653.22	4338.00	4784.43	5225.35
3301.81	3705.88	4361.87	4812.01	5229.52
3307.64	3940.91	4412.82	4832.23	5238.76
3322.32	3969.42	4438.22	4855.27	5257.12
3330.15	3970.15	4480.96	4868.92	5451.08
3351.35	4030.45	4531.54	4869.41	5481.15
3366.43	4032.51	4607.52	4872.66	5486.37
3380.89	4077.88	4678.39	4876.35	5504.48
3464.58	4161.95	4722.42	4892.20	5522.02
3475.01	4215.66	4729.93	4962.45	5535.01
3477.33	4305.60	4742.07	4968.11	5540.28
3499.40	4308.49	4755.59	4971.85	5543.49
3504.70				

Barium Chloride.

When barium is present, the arc has a large round center, which shades from rose pink through lemon yellow to lime green at the edge. Next to each carbon it is of a brilliant lemon yellow color. The carbons are not very highly heated.

The barium lines come out easily, and are very strong; but the bands and all but the strongest lines in the original spectrum are so weak that they are almost invisible.

Barium lines photographed.

λ = 2304.32	λ = 3662.62	λ = 4085.35	λ = 4407.10	λ = 4636.80
2335.33	3664.76	4087.90	4413.96	4642.38
2596.89	3689.28	4110.46	4432.13	4673.69
2702.78	3701.87	4130.88	4467.36	4691.74
3281.96	3794.77	4132.60	4489.50	4700.64
3357.00	3861.87	4166.24	4493.82	4724.98
3420.48	3889.45	4179.57	4506.11	4726.63
3501.29	3891.97	4224.11	4523.48	4877.99
3525.23	3892.97	4239.91	4525.19	4900.13
3544.94	3900.54	4242.83	4554.21	4903.11
3577.79	3906.20	4264.45	4574.08	4934.24
3579.97	3910.04	4283.27	4579.84	4947.50
3586.64	3917.42	4323.15	4589.82	5424.82
3588.33	3935.87	4325.38	4591.88	5437.66
3593.58	3938.09	4333.04	4600.02	5519.37
3599.60	3993.60	4350.49	4605.11	5535.69
3611.17	3995.92	4359.80	4620.19	5777.84
3637.10	4079.56	4402.10	4628.45	5853.91

Zinc Chloride.

The band spectrum is better than was obtained under any other circumstances. The bands are greatly extended and very distinct. The arrangement of lines in different parts of the arc is especially marked in the flame spectra. All of the calcium and aluminium lines are very clear in the outer sheath of the arc and near the negative carbon. The bands cling closely to the positive carbon, but the zinc lines cross the arc with nearly equal brilliancy in all parts. Only the carbon bands are seen in the region having a wave length greater than $\lambda = 4862$.

The "grating effect" is continuous from $\lambda = 3400$. to $\lambda = 5635$. The effect of the zinc seems to be to obscure all but the strongest of the other metallic lines, and to increase the intensity of the band spectrum.

Zinc lines photographed.

$\lambda = 2802.11$	$\lambda = 3072.19$	$\lambda = 3515.26$	$\lambda = 4293.02$
2823.27	3075.99	3572.90	4298.54
2833.13	3282.42	3671.71	4630.06
2863.43	3302.67	3683.63	4680.38
2873.39	3303.03	3740.12	4722.26
2913.63	3345.13	4019.75	4810.71
3018.50	3345.62	4058.02	5182.20
3035.93	3346.04	4101.94	

Cadmium Chloride.

The spectrum obtained when cadmium is present in the arc is similar to that with zinc.

Cadmium lines photographed.

$\lambda = 2677.65$	$\lambda = 2961.64$	$\lambda = 3466.33$	$\lambda = 3981.92$
2712.65	2980.75	3467.76	4306.98
2733.97	2981.46	3500.09	4413.23
2763.99	3081.03	3595.64	4662.69
2775.09	3133.29	3610.66	4678.37
2837.01	3252.63	3613.04	4800.09
2868.35	3261.17	3649.74	5086.06
2880.88	3299.11	3729.21	5154.85
2881.34	3403.74		

Copper.

Copper gives an arc which has a bluish-green center with bright green near the carbons. This is surrounded by a dark part, which is again enclosed by a yellow outer sheath.

The spectrum appears almost like that obtained from the center of the original arc, with the addition of the lines due to copper. The variation in brightness of certain lines at the positive and negative carbons is very noticeable, and is more easily observed owing to the fact that the copper lines are all strongest *about half-way between the carbons,* at which point they show a decided enlargement. In the band spectrum only the fine, grating-like lines are seen. The indications of the strong lines are seen at the negative carbon, while the lines of the band spectrum are strong for the whole width of the arc.

Copper lines photographed.

$\lambda = 3771.96$	$\lambda = 4123.38$	$\lambda = 4378.40$	$\lambda = 4674.98$
3860.64	4177.87	4397.42	4697.62
4003.18	4242.42	4415.79	4704.77
4010.96	4249.21	4480.59	5105.75
4015.80	4253.53	4507.62	5144.35
4022.83	4259.63	4509.60	5153.33
4056.80	4267.48	4513.39	5218.45
4062.54	4275.32	4531.04	5220.25
4063.50	4329.00	4539.98	5292.75
4073.28	4336.17	4587.19	5700.39
4080.70	4354.91	4651.31	5782.30

Silver.

The appearance of silver in the arc, and its effect upon the spectrum, are almost identical with that of copper.

Silver lines photographed.

$\lambda = 3280.80$	$\lambda = 3841.30$	$\lambda = 4055.44$	$\lambda = 4616.03$
3383.00	3907.63	4212.10	4668.70
3542.67	3914.47	4311.28	4678.04
3557.30	3940.30	4379.45	5209.25
3681.80	3943.10	4396.49	5465.66
3710.10	3981.87	4476.29	5471.72
3810.60	3991.90	4556.13	

Remarks.

As has been noted in a previous paragraph, the lines of the ordinary arc which are strongest at the negative carbon increase in intensity in the outer sheaths, while the reverse is true with the lines from the positive carbon. When the metals K, Na, Li, Ba, Sr, and Ca are introduced, the lines from the positive carbon are weakened. The effect is most marked in the case of potassium. Barium reduces the carbon bands the most.

The metals Cu and Ag, from the group I. *b*, give the spectrum in about its normal condition, with the lines due to the especial metal added; while the metals Cd and Zn increase the intensity of the bands and diminish the strength of the metallic lines originally present near the negative pole.

It has been frequently observed by others who have worked with metallic spectra by this method, that it is necessary to have added resistance in the circuit which supplies the arc, when metals are used, in order to maintain a constant length of arc. The amount that had to be added in the course of these experiments varied very much with the different metals.

In a circuit of such electromotive force that 3 ohms resistance were necessary to give the ordinary arc its normal voltage (48 v), it was found that the following resistances would restore the arc to its proper condition:

Metal.	Resistance.	Metal.	Resistance.
Silver	3.1	Cadmium	5.8
Copper	3.8	Potassium	9.1
Zinc	5.6	Sodium	9.5
Barium	5.6	Lithium	9.7
Strontium	5.8	Calcium	9.9

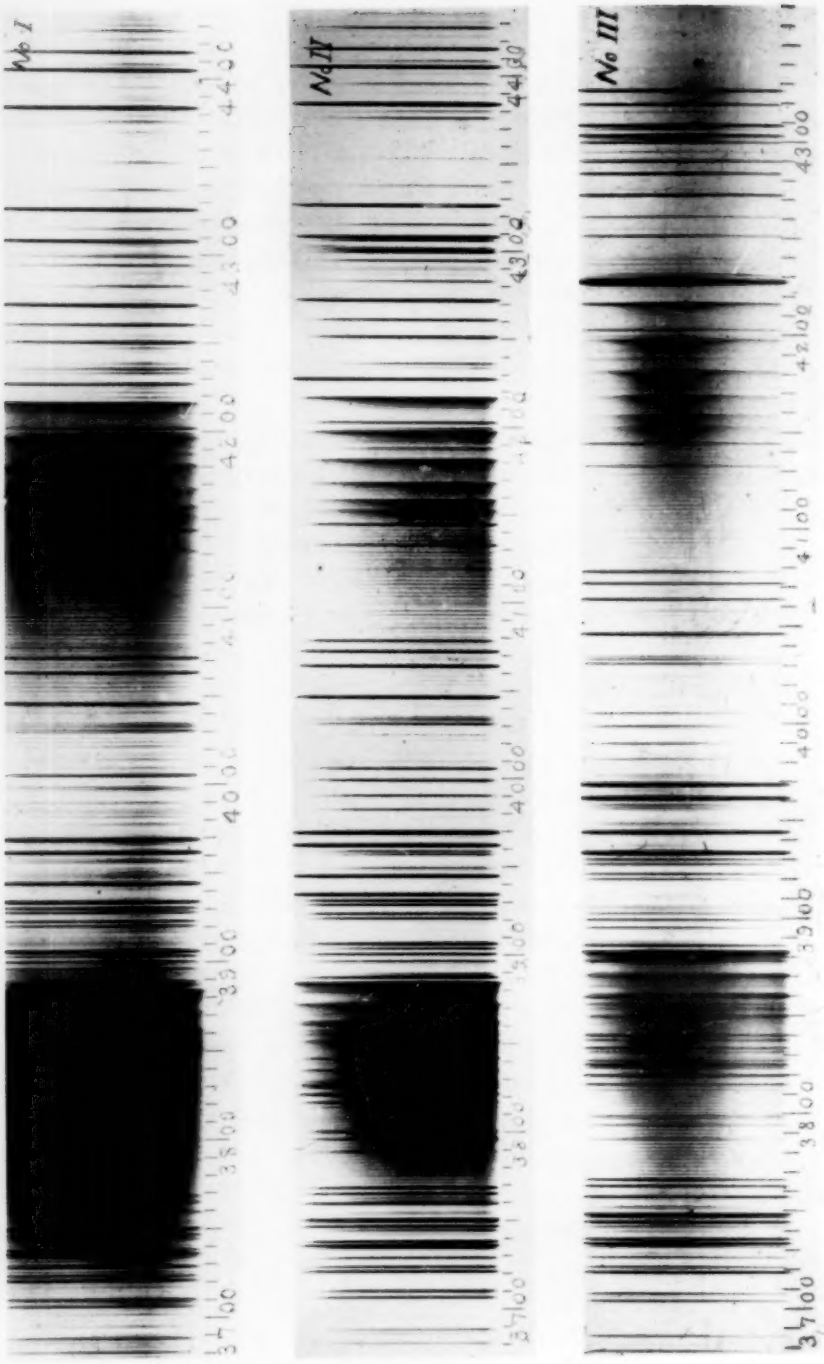
When the metals were used, the temperature of the carbons was apparently much less than with the pure carbon points. The temperature of the positive carbon was most affected, and it did not waste so rapidly in proportion to the negative as when no metallic salt was in the core.

It might be thought that the changes observed were due to the fact that the temperature is not high enough to render all the lines visible. This view would be strengthened if the lines of metals which require the highest temperature for fusing and vaporization were strongest in those parts of the arc which are hottest. But this does not seem to be the case, for although K, Na, and Li, metals of low melting points, are strengthened at the negative carbon, so also are Ba, Sr, and Ca, which have relatively high melting points. The Cu and Ag lines extend across the arc with nearly even intensity, and the same is true of Zn and Cd.

It does not seem that the diminished intensity of the carbon bands in the presence of certain metals can be wholly due to the density of the gases of the flame; as there is no direct relation between the amount of weakening of the bands and the density of the metallic vapor. Neither does the change seem to depend in any simple way upon the atomic weight of the metals. Barium and potassium obscure the bands most; and they are respectively the highest and lowest in atomic weight of the metals studied.

There are many reasons for believing that there is an electrolytic action in the arc. This belief is strengthened by the fact that the metallic lines appear at the negative carbon, and the carbon bands are strongest at the positive. It is also true that the metals K, Na, Li, Ba, Sr, Ca, which are highly electropositive, are more strengthened at the negative carbon than are Cd, Zn, Cu, Ag, which are less positive.

In studying the effect of the metals upon the lines of the original spectrum, we may consider the need of increased resistance in the outer circuit to be due to diminished resistance of the arc, or to a change in the counter electromotive force. In the former case, the list of resistance given should have the same order as the resistance of the various metallic vapors. The arrangement, however, is not that of the respective metals as we know them at ordinary temperatures.



C. W. BALDWIN ARC SPECTRA.

Summary.

(1) The spectrum obtained from the electric arc is not the same for all parts of the arc and the surrounding flame. On the contrary, there is a decided difference in the spectrum of the several sheaths. The difference is largely due to a fading out of the carbon bands and of all lines from the positive carbon, and an increase of intensity in the outer sheath of those lines which are most brilliant near the negative carbon. Certain lines and bands which are invisible in the center are seen in the outer part of the flame.

(2) The total number of metallic lines diminishes rapidly, as we explore the arc from the center outwards.

(3) When the spectrum is changed by the introduction of metals into the carbons, it is observed that the more positive metals, such as K, Na, Li, and Ba, Ca, Sr, greatly weaken, but do not destroy, the characteristic band spectrum of the arc. The lines which are most affected by these metals are those which in the ordinary spectrum are strongest near the *positive carbon.*

Certain metals, as silver and copper, do not materially alter the original arc spectrum, while others, as zinc and cadmium, affect the lines near the *negative carbon,* and thus give the band spectrum, which is no longer obscured by the metallic lines usually present, an unwonted brilliancy.

The causes of the phenomena are not easily discovered, but it is hoped that the points brought out in this paper may throw some light upon the intricacies of this complex problem.

MINOR CONTRIBUTIONS.

A METHOD FOR THE USE OF STANDARD CANDLES IN PHOTOMETRY.

BY CLAYTON H. SHARP.

THE fundamental assumption on which is based all American and English practice in the use of candles as a standard of light in photometry is that the intensity of light emitted by a candle is, within certain arbitrary limits, proportional to the rate at which the material of the candle is consumed. Supposing this assumption to be in a measure justifiable, we could scarcely imagine it to be rigorously exact. The purity and hygrometric state of the air, which Liebenthal [1] has recently shown to have such a large influence on the intensity of the Hefner light, can scarcely be of inappreciable influence on the candle flame.[2]

But no matter how nearly this assumption approximates to the true state of affairs, the fundamental and inevitable difficulty with this definition of the light unit still remains. It is this: what we ought to know is not the mean rate of consumption during the period over which the measurements extend, but the rate at the instant at which a photometer setting is made. Since it is impracticable to determine this quantity, the mean rate has been used for correcting observations.

That this cannot be a proper method of procedure on the assumption made, is shown by a study of the enormous and quick variations to which the quantity of light emitted by a candle is subject. Curves [3] showing these instantaneous variations have been obtained by the use of a sensitive bolometer which, when exposed to the radiation of a candle flame, would respond to every change in the intensity of that radiation. It is quite

[1] Liebenthal, "Ueber die Abhängigkeit der Hefnerlampe und der Pentanlampe von der Beschaffenheit der umgebenden Luft."

Elektrotechnische Zeitschrift, XVI., p. 655, 1895.

Zeitschrift für Instrumentenkunde, 15, p. 147.

Electrical World Digest, XXVI., p. 220 and p. 500, 1895.

[2] For evidence confirming this statement see an article by John Methven read before the Southern District Association of Gas Engineers and Managers, London Gas World, 1889, p. 572. A translation into German will be found in Dingler's Polytechnisches Journal, 1890, Vol. 277, p. 276.

[3] Sharp and Turnbull, "A Bolometric Study of Light Standards," PHYSICAL REVIEW, Vol. II., p. 1. This article will be referred to frequently.

possible that a series of photometric settings should be made in such a way that their mean would give a value considerably lower than the mean ordinate of an intensity curve covering all the time between two weighings of the candle.

Moreover, in the bolometric investigation it was found that corrections to the mean ordinates of the various curves for deviations from the normal rate of consumption did not serve to reduce these ordinates to a common value; or, in other words, that the energy radiated was not proportional to rate. Since the radiant efficiency of a candle flame does not change with its size, — provided that it does not smoke, — this would be true for luminous radiation as well as for total radiation. This is in accord with the observations of Tyndall[1] and the results of von Jolly, who showed that on a mountain summit candles have a shorter flame and diminished intensity, with the same rate of consumption.

Recognizing these facts, the German photometrists have insisted that the flame height is the significant factor, and that candle measurements should be made only with a standard height of flame. They would clean the wick of the candle, wait until the flame height becomes normal, and then set the photometer.[2]

There are certain objections to this method of procedure although it undoubtedly gives better results than the English practice. In the first place, it must be a time-wasting and patience-trying operation. Moreover, it is very doubtful if snuffing the wick of a standard candle is an allowable operation, since the shape of the flame depends on the particular curl which the wick assumes, and is normal only when the wick has its natural curl.

A more desirable method would be to measure, at the instant the photometer setting is made, the height of the candle flame; then, knowing a relation between the height of the flame and the intensity of light emitted, to reduce the instantaneous intensity to the intensity at normal flame height.

The first question then becomes: Does any definite relation exist between these quantities? Giroud has shown that the slender, pointed flame

[1] Tyndall, "Heat as a Mode of Motion." Also Dr. Frankland, Philosophical Transactions, 1861.

[2] In the original directions for the proper use of the German Vereinskerze, however, it is stated that snuffing is unallowable, and that measurements should be made only when the quietly burning flame has reached a height of 50 mm. See "Beschluss der Versammlung des Vereines des Gas- und Wasserfachmänner Deutschlands," etc. Dingler's Polytechnisches Journal, 206, p. 329. This is a reprint from the Journal für Gasbeleuchtung und Wasserversorgung, 1872, Nov. 12.

On the other hand, see the report of a committee of the Verein von Gas- und Wasserfacmännen as transcribed in La Lumière Électrique, 34, p. 178. Here snuffing the wick is recommended. See also Krüss' book, Elektrotechnische Photometrie.

of his bec-bougie varies at the rate of about 2 per cent per millimeter, the relation between flame height and intensity being nearly linear. Liebenthal[1] has drawn curves (see Fig. 1) showing this relation in the case of the Hefner lamp and of the English standard candle. For the former the relation is approximately linear for small variations and shows for variations between 35 mm. and 45 mm., 2.6 per cent per millimeter. The two English candle curves are practically straight lines for all ordinary variations, and show 2.1 per cent and 1.9 per cent per millimeter respectively, for variations between 40 mm. and 50 mm.

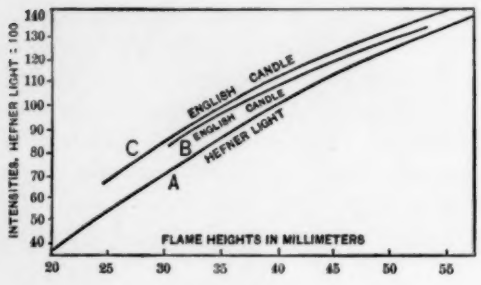


Fig. 1.

Curves by Liebenthal.

The present experiments were suggested by the results of the bolometric tests of candles. They were undertaken first for the purpose of investigating this relation between flame height and intensity, and, second, to determine whether the use of this relation would not make it possible to get more consistent results than can be obtained by correcting for rate of consumption.

Two methods were employed to determine the flame height-intensity ratio. In the first method the intensity of the radiation of the candle was measured by the bolometer in the way previously described. To measure the height of the flame, a long camera was constructed, having its lens and ground-glass plate at a fixed distance from each other. The ground-glass plate was graduated empirically to read directly in millimeters the height of objects focussed upon it. The candle was placed on a pan attached to a spiral spring of such a length that its elongation would be just equal to the length of the candle. By this arrangement the top of the candle was kept at a constant height above the floor, and when once the image of the base of the flame had been accurately adjusted on one of the lines of the camera screen (to facilitate which the screen was capable of a slight vertical movement), it remained there during a considerable period of time. Hence, to measure the height of the flame at any instant, it was necessary only to glance at the image of the *top* of the flame and to note its position on the screen. It will be noticed that this camera device is, to a certain extent, a modification of Krüss' optical flame measure which has been in use a

[1] Liebenthal, "Photometrische Untersuchungen über die von Hefner-Altensck'sche Lichteinhert," Elektrotechnische Zeitschrift, 9, p. 96, 1888.

number of years. Extended to take in the bottom of the flame, and combined with the spring balance, it enables measurements to be made with great quickness, and with a sufficient degree of accuracy, by an observer who is located so far from the flame as to leave it entirely undisturbed by his movements.

The magnifying power employed was about two, and heights were measured only to 0.5 mm. Greater closeness of measurement was deemed unnecessary on account of the ill-defined nature of the base and tip of the flame. The actual base of a candle flame is difficult to observe, on account of the small quantity of light which it emits. The procedure adopted was to set on the line of demarkation between the charred and uncharred portions of the wick, since this was found usually to mark the base of the flame. In case a close inspection of the candle showed the base of the flame to be slightly above this point, a further adjustment of the screen was made.

In order to insure great steadiness of the flame, the candle was placed in a roomy, well-ventilated box having a glass window. Having put the candle in position before the bolometer, and having adjusted the camera properly, the bolometer screen was raised and simultaneous observations were made of galvanometer deflections and flame heights. These readings were corrected for any change in sensitiveness of the bolometer and any drift of the galvanometer needle, and were plotted, using flame heights and galvanometer deflections as coördinates.

In the second method a Lummer-Brodhun photometer was used. At one end of a photometer bar 200 in. long was placed a 110-volt glow-lamp. This was maintained at a voltage of 100 by means of a storage battery. Being run at low efficiency, its color was about the same as that of a candle, and its change in candle power during the time it was in use was too small to be detected.

At the other end of the bar was the candle, supported by its adjusted spring. The candle was always placed so that the curl of the wick was perpendicular to the axis of the bar.[1] The arrangement for measuring flame heights is shown in Fig. 2, which represents a projection of the apparatus on a horizontal plane. *B* is the photometer bar, *C* the candle, *M* a mirror placed behind the candle in such a way as to reflect the rays from it through the lens *L*, which projected them on a graduated screen *S* placed immediately behind the bar. The mirror was carried on a movable support so as to admit of an adjustment of focus.

This arrangement was adopted, since by its use one observer could do

[1] For the variation of the intensity of candle as a function of the azimuth of the plane of the wick, see Methven, *loc. cit.;* also an article by Sugg, in the Journal for Gas Lighting, which is reprinted in the Scientific American Supplement, No. 484, p. 7726.

all the work. The method was simply to make a rather quick photometer setting, and then instantly to note the position of the top of the flame on the screen, reading the position of the photometer afterwards.

In some of the earlier measurements a kerosene lamp with an Argand burner similar to the ordinary student-lamp burner was used as a secondary standard. The upper part of the chimney was covered by a closely fitting cylinder of ferrotype iron in such a way that the top of the flame was entirely hidden. This furnished a very steady source of light after it had been burning long enough for the parts to become thoroughly warmed, and

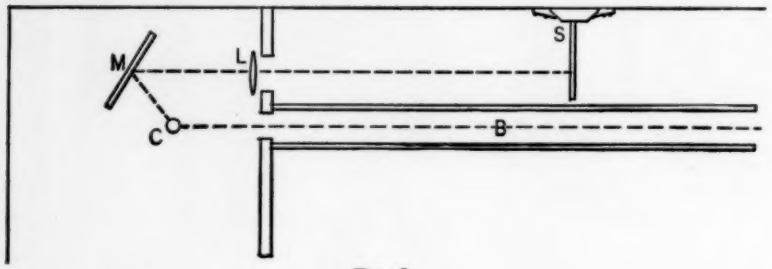


Fig. 2.

Arrangement of Photometer.

its intensity was unaffected by slight adjustments of the height of the flame, provided only that the flame was always high enough. Unfortunately, its intensity varied enough from day to day to make its indications unreliable without a daily calibration, and it was replaced by the more convenient and accurate glow-lamp. Observations of variation of intensity with flame height are not affected by this fact.

The observations were treated in the following manner: The various observed values of flame height were collected in such a way that heights of 41.0 mm., 41.5 mm., and 42.0 mm., formed one group; 42.5 mm., 43.0 mm., and 43.5 mm., another, etc. The mean height of each group was found, and also the mean bar-reading corresponding to it. The candle power of the standard was found by taking the mean of all the heights and bar-readings, and reducing, by means of an approximate correction, to a standard flame height of 45 mm. Using this value for the intensity of the glow-lamp, the intensity of the candle corresponding to each group was computed. By means of a curve plotted from these values the percentage variation per millimeter of flame height was determined.

In order to find the relative accuracy of this and of the ordinary method of using candles, the following observations were made: A candle burning normally was weighed by the "method of transits," was transferred to the spring balance, and ten or more photometer settings made — the flame

heights also being noted. The candle was then weighed again, and another group taken. A number of such sets of observations were made on several days, and since the glow-lamp was used as a reference standard, these sets are comparable with each other.

The mean value of the candle power of the glow-lamp given by each of these sets of observations was corrected for rate in the ordinary way, and was also corrected by reducing from the mean flame height to the standard height of 45 mm., using the mean value of the relation between intensity and flame height as determined from all the observations, both bolometric and photometric. The deviation of each value obtained for the candle power of the glow-lamp from the mean value obtained from all the observations was computed, and this deviation was reduced to per cent. A comparison of the percentage deviations given by the two methods shows their relative accuracy, while the absolute values of the percentages show the error which one is liable to make in using candles in either of the two ways.

TABLE I.

Flame height (mm.).	Galvanometer deflection.	Flame height (mm.).	Galvanometer deflection.	Flame height (mm.).	Galvanometer deflection.
48.0	29.0	44.0	26.7	43.0	25.8
48.5	29.5	45.0	27.5	44.0	27.0
49.5	30.3	45.5	28.3	Wick of candle cleaned.	
48.0	29.2	43.5	27.0		
47.0	28.2	43.5	27.0	55.0	37.2
47.5	28.8	44.5	27.5	46.5	30.6
45.5	27.5	44.5	27.5	47.5	31.3
46.5	28.0	45.0	28.3	48.0	32.0
46.5	28.2	44.5	27.7	49.0	32.7
46.5	28.0	43.5	26.5	49.0	32.6
45.0	27.0	43.5	27.0	49.5	32.8
45.5	27.6	43.0	26.5	50.5	33.7
45.5	27.8	42.5	26.0	50.0	33.0
44.5	26.5	43.5	26.8	50.0	33.0
42.0	25.8	42.5	25.5	50.0	33.2
43.0	26.8	43.5	26.0	49.0	32.6
43.0	26.0	44.0	26.3	47.0	30.4
43.5	26.7	43.5	26.0	48.5	30.0
44.0	26.8	43.5	26.2	48.5	31.0
44.5	27.1	44.0	26.7	47.0	30.0
44.5	27.2	44.5	27.0	46.5	30.0
43.5	26.4	44.0	26.8	46.5	30.0

TABLE II.

Flame height (mm.).	Photometer bar.	Flame height (mm.).	Photometer bar.	Flame height. (mm.).	Photometer bar.
45.5	702	41.5	713	53.0	686
46.5	699	43.0	707	48.0	700
48.0	700	43.0	708	48.5	695
49.0	693	44.0	706	46.0	704
51.5	690	44.0	707	45.0	708
53.0	697	45.0	705	44.0	707
44.5	709	44.0	709	44,0	711
46.0	705	44.0	710	46.0	707
49.0	694	43.0	713	43.0	713
46.0	699	45.0	708	46.0	708
48.0	698	End of	wick	44.5	710
48.0	693	cut	off.	44.0	711
49.0	691	40.0	712	46.0	711
45.5	700	44.0	708	45.5	708
44.0	707	47.0	698	46.0	712
45.5	699	48.0	696	42.5	716
48.0	697	50.0	693	42.0	715
46.0	698	54.0	688	43.0	715
46.5	696	53.0	688	44.0	714
45.0	700	51.0	693	45.0	711
45.0	701	50.0	694		

TABLE III.

Bolometric.		Per cent.	Photometric.		Per cent.	Photometric.		Per cent.
1894. Nov. 29 . .		2.2	1895. July 27 . . .		3.3	1895. Dec. 3	E	2.3
Dec. 5 . . .		2.7	Oct. 30 . . .		3.4		F	
1895. Feb. 23,	I.	2.2	Nov. 1	I.	3.3		G	
	II.	2.5		II.	3.3		H	
	III.	3.2	Nov. 6	I.	2.2	Dec. 4	I	2.6
March 21,	I.	3.1		II.	2.7		J	
	II.		Nov. 27	I.	2.7		K	
Oct. 4 . . .		2.7		II.	2.9		L	
			Dec. 2, A.M.,	A	2.7		M	
				B			N	
			Dec. 2, P.M.,	C	2.8			
				D				
				D′				
Mean . . .		2.7				Weighted mean of all		2.7

TABLE IV.

Name of group of observations.	Rate (grams per hour).	Flame height (mm.).	C. P. of glow-lamp uncorrected.	C. P. corrected for rate.	C. P. corrected for flame height.	Deviation from mean corrected for rate.	Deviation from mean corrected for height.	Percentage deviation. Rate.	Percentage deviation. Height.
								%	%
A	7.601	43.0	6.11	5.99	5.78	+0.35	+0.04	+ 6.0	+0.7
B	8.320	45.15	5.785	6.20	5.80	+0.56	+0.06	+ 9.8	+1.0
C	6.981	44.95	6.01	5.41	6.00	−0.23	+0.26	− 4.25	+4.5
D	8.100	46.1	6.09	6.35	6.25	+0.71	+0.51	+12.6	+8.7
E	7.157	46.4	5.52	5.09	5.73	−0.55	−0.01	− 9.8	−0.2
F	7.863	44.7	5.67	5.74	5.62	+0.10	−0.12	+ 1.6	−2.1
G	8.030	44.8	5.72	5.91	5.69	+0.27	−0.05	+ 4.8	−0.9
H	7.330	44.05	5.80	5.47	5.66	+0.17	−0.08	+ 3.0	−1.4
I	8.422	44.3	5.65	6.13	5.54	+0.49	−0.20	+ 8.5	−3.5
J	7.271	47.1	5.35	5.02	5.65	−0.62	−0.09	−11.0	−1.6
K	7.367	46.15	5.50	5.22	5.67	−0.42	−0.07	− 7.6	−1.2
L	7.440	45.6	5.64	5.41	5.73	−0.23	−0.01	− 4.25	−0.2
M	7.137	42.3	6.00	5.52	5.56	−0.12	−0.18	− 2.3	−3.2
N	7.301	44.2	5.79	5.45	5.67	−0.19	−0.07	− 3.5	−1.2
Means, disregarding signs	7.594	44.9	5.76	5.64	5.74	0.36	0.125	6.35	2.16
Nov. 6, I.		45.5	5.60		5.68		−0.09		−1.6
II.		46.3	5.79		6.00		+0.23		+4.0
Nov. 11		43.1	6.17		5.85		−0.08		−1.4
Nov. 12, I.		44.1	5.87		5.73		−0.04		−0.7
II.		42.9	6.20		5.85		−0.08		−1.4
Dec. 2, D′		49.3	5.36		5.99		+0.22		+3.8
Means of all, disregarding signs		45.0	5.78		5.77	Last six only.	0.123		2.14

Results.

Table I. gives a characteristic set of data obtained by the use of the bolometer, 1894, March 21. Table II. is a similar set of photometric data obtained 1895, November 6. The data of Table I. and Table II. are shown reduced and plotted in Fig. 3 and Fig. 4 respectively. Table III. gives values found for the variation in intensity of candles expressed in per cents per millimeter. Table IV. shows, in the way described above, the comparative accuracy of the two methods of reducing candle observations. Figure 5 shows plots obtained from groups of observations

designated by *A, B, C, · · · N.* Figure 6 shows plots from three successive sets of bolometric observations.

An inspection of the tables and curves will show that while the relation between flame height and intensity is a fairly definite one for any given

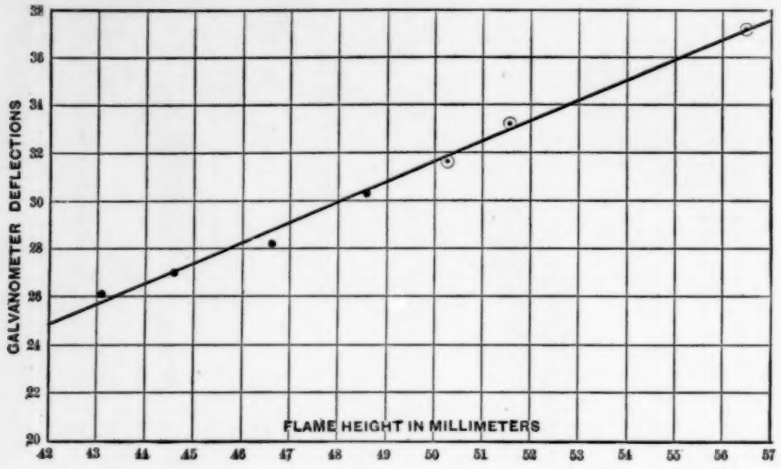


Fig. 3.

Bolometer Curve.

group of observations, there is a considerable range of variation in the values for it as obtained from different groups. Moreover, the relation sometimes changes during one burning of the candle. Figure 6 illustrates this peculiarity in that there is a group of points marked ⊡ which lie considerably below the line plotted to represent all the observations; and that the slope of the flame height-intensity curve plotted from the points

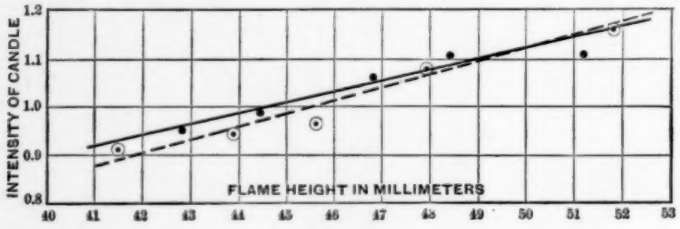


Fig. 4.

Photometer Curves.

marked ⊡ is materially different from that obtained from other groups of points. This may be due to a change in the shape of the wick. The fact that this relation is not absolutely constant does not vitiate the proposed method of treating candle observations; for since the deviations of

flame height from 45 mm. is seldom more than 10 per cent, if our assumed value for this relation is in error by as much as 20 per cent, our reduced value for candle power would be in error by no more than 2 per cent.

Table IV. shows that the mean deviation from the mean of observations

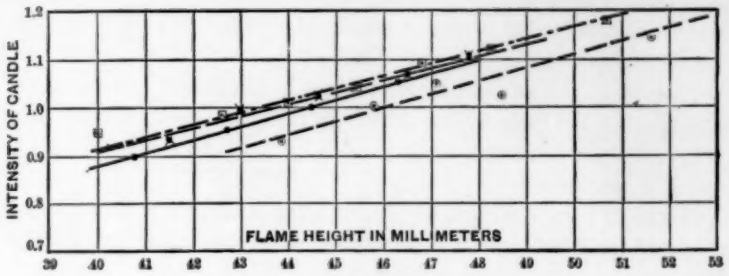


Fig. 5.

Photometer Curve.

corrected in this way is a little over 2 per cent, and that fourteen out of twenty values were in error by 2.1 per cent or less. In the case of corrections for rate, the mean deviation is over 6 per cent, while but one out

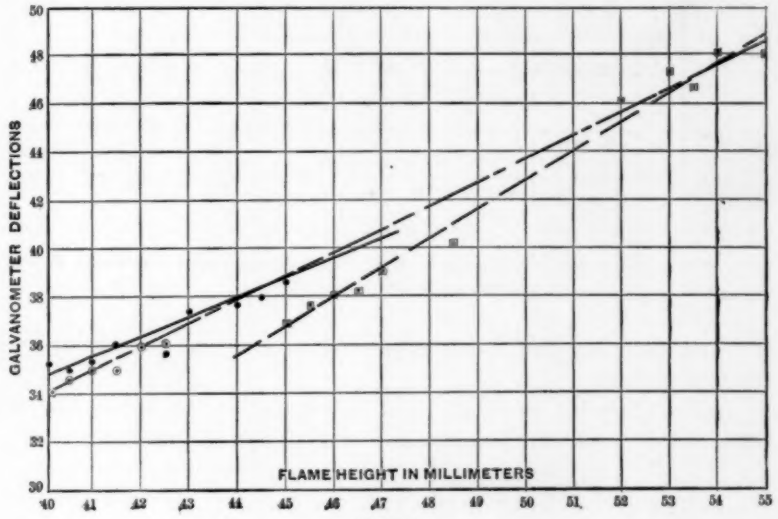


Fig. 6.

Bolometer Curve.

of fourteen values deviated by less than 2 per cent, and only four by less than 4 per cent.

In other words, by correcting for flame height an error of less than 2 per cent may reasonably be expected, and the probability of making an

error greater than 4 per cent is small; while in correcting for rate, errors of 8 per cent and 9 per cent are of common occurrence.

The values corrected for rate might, perhaps, be more consistent if the rule were followed to reject all observations in which the rate fell below 114 or above 126 grains per hour. Similarly, the errors in the values corrected for flame height might be smaller if observations made at extreme flame heights were to be rejected. Indeed, it is one of the chief advantages of the method that the observed flame height furnishes a criterion for the rejection of any observation which is regarded as doubtful. In this discussion, however, in order to be equally fair to both methods, no observations have been rejected.

The results of these photometer observations confirm fully those obtained by the use of the bolometer in determining the variations of light standards, and show very conclusively that the fundamental assumptions on which the bolometric tests were based, were entirely justifiable. If we compute from Table IV. the mean value of the flame height-intensity ratio, as determined

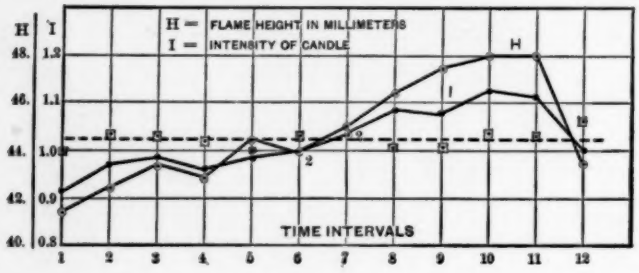


Fig. 7.

Variation of flame-height (*H*) and intensity (*I*) of English candles. Dotted line shows intensity reduced to standard flame-height.

by the bolometer, we find that it is just the same as the mean value from *all* the observations.

In the "Bolometric Study of Light Standards" it was shown that the English candle is subject to sudden variations in intensity which are sometimes as large as 15 per cent. Many of these sudden drops were noticed while making the photometer observations, and they all had the same characteristics as are shown by the bolometer curves. Figure 7 shows a group of these observations — group F in the tables. Assuming that the time intervals between the various photometer settings were equal, points were plotted showing the relation between intensity of the candle and time and between flame height and time. It will be seen at once that the two curves are of very similar characters. The flame height gradually increased,

and with it the intensity, until, when the height of 48 mm. had been reached, there was a sudden drop, the change in intensity amounting to 12 per cent.

These curves evidently show in an imperfect way variations precisely similar to those which are so faithfully reproduced by the galvanometer needle. In view of these qualitative and quantitative results, it would seem to be impossible to doubt the reliability of the bolometer as an instrument for making such tests.

Another interesting consequence of these candle measurements is the very careful standardization of the glow-lamp. Its intensity has been measured in terms of the Hefner light also, and by this means a good determination has been made of the candle power of the Hefner light. This result, together with previous determinations of the same ratio, appears in Table V.

TABLE V.

Observer.	Hefner.
	English candle.
Sharp, candles reduced for rate	0.872
Sharp, candles reduced for flame height	0.892
Sharp and Turnbull, integration of energy curves [1]	0.941
Violle	0.98
Reichsanstatl investigations, mean value [2]	0.876
Netherland Photometry Commission [3]	0.921
S. Schiele, mean value [4]	0.881

The value 0.94 is taken from curves made in the bolometer tests, and rests on the assumption that the radiant efficiencies of the candle and Hefner flames are equal. Since the Hefner flame is distinctly redder in color than the candle flame, its radiant efficiency is probably smaller, and consequently the value 0.94 is too large. A difference in the radiant efficiencies of the two sources of less than 0.2 per cent would serve to bring

[1] *Loc. cit.*

[2] This is the mean of a long series of determinations made by different observers at different times, using candles from various sources. The measurements were taken at normal flame height of 45 mm. See "Beglaubigung der Hefnerlampe"; Zeitschrift für Instrumentenkunde, 13, p. 257.

[3] An abstract in German by Krüss will be found in the Journal für Gasbeleuchtung und Wasserversorgung, 1894.

[4] Schiele, Report of Committee on the Comparison of the Hefner lamp and German and English candles, Journal für Gasbeleuchtung und Wasserversorgung, Band 32, 1889, p. 757; also Dingler's Polytechnisches Journal, 274, p. 540. The measurements were made at normal flame height of 45 mm.

this value down to 0.88. The preponderance of evidence in favor of the value 0.88 is very great. It is probably true that the very best way we have at the present time of determining candle power is to use the Hefner lamp and then to reduce by the use of this ratio.

The writer desires in conclusion to express his obligations to Mr. C. P. Matthews for timely assistance in making some of the above observations.

CORNELL UNIVERSITY, ITHACA, N.Y.,
January, 1896.

THE GRAPHICAL REPRESENTATION OF MAGNETIC THEORIES.

By HAROLD N. ALLEN.

THE induction theory of magnetism, introduced by Faraday, is now looked upon by all physicists as correct. The older theory which assumes the existence of magnetic fluids covering the ends of the magnet is in some cases mathematically simpler, and is for this reason often made use of. This, however, is apt to breed confusion as to the true nature of the induction or polarization in any given case. The difficulty Tyndall experienced in accepting Faraday's views as to diamagnetism, is accounted for by the fact that he was thinking in terms of the fluid theory, while Faraday was considering the magnetic polarization in the diamagnetic substance.

The object of this paper is to insist again upon the distinction between these two theories, and at the same time to consider some points in the induction theory itself. A number of diagrams will be described which illustrate the different aspects of the induction theory. They show how the molecules of the magnet are supposed to be polarized, and how this polarization is continued in the surrounding ether. The tubes of force, or "polarization tubes," and the equipotential surfaces are drawn in each case according to Maxwell's method. The figures must be revolved about the horizontal axis, so that the lines drawn will trace out, some the bounding surfaces between the tubes, and others the equipotential surfaces.

It has been found convenient to give the name polarization tube to a tube of force consisting of a bundle of 4π induction tubes. The polarization at any point is measured by the number of polarization tubes passing through a square centimeter of a surface, which cuts them at right angles, just as the induction is measured in the same way by means of the induction tubes.

If D_m is the magnetic polarization,
B_m the magnetic induction,
H_m the magnetic field intensity,

the following relations will hold:

$$D_m = \frac{B_m}{4\pi} = \frac{\mu H_m}{4\pi}.$$

A polarization cell or energy cell is a portion of the medium bounded on the sides by the walls of a polarization tube, and at the ends by two equipotential surfaces, differing from one another in value by unity. It is possible to regard each of these cells as containing half a unit (erg) of energy. This energy is to be regarded as in some way directed along the lines of force, as the energy of a bullet is directed along the line of its flight, or the energy of rotation of a fly-wheel is directed along its axis.

The length of the cell in a uniform field being

$$\frac{1}{H_m} = \frac{\mu}{4\pi D_m} = -\frac{dn}{dV_m},$$

and the area of its section being $\frac{1}{D_m}$,

the volume will be $\frac{\mu}{4\pi D_m^2}$.

Thus the density of the directed energy is $2\pi D_m^2$ in a medium of unit permeability.

According to one statement by Maxwell, the energy density in a medium of permeability μ is $\frac{2\pi D_m^2}{\mu}$. Ampère's theory of magnetism, however, implies, as will be shown, a much larger energy density than this.

In the first part of his treatise, Maxwell seems practically to assume that the polarization in a paramagnetic substance is made up of two parts, the polarization of the iron molecules or the intensity of magnetization I, and the polarization of the ether which occupies the same space $= D' = \frac{H'}{4\pi}$, where H' is the field intensity in the substance; that is, in a long uniform crevice, the direction of which coincides with that of the induction tubes.

Thus the total polarization is

$$D_m = \frac{H'}{4\pi} + I,$$

or

$$D_m = D' + I,$$

or in more familiar terms,

$$B_m = H' + 4\pi I.$$

The two polarizations are regarded as being superimposed, so that in some way they occupy the whole of the same space at the same time.

In Diagram II., Fig. 1, are shown the equipotential surfaces and polar-

ization tubes produced, when an infinite cylinder of constant permeability, $\mu = 2$, is placed with its axis parallel to a uniform field of force $H = 1$.

Diagram I., Fig. 1, is a representation of the field before the introduction of the cylinder. The polarization tubes in these diagrams are bounded by the cylinders generated by the horizontal lines when the figure is rotated about AB. The line CD traces out the surface of the paramagnetic cylinder. The equipotential surfaces in the cylinder are simply continuations of those in the outside field. The polarization tubes are twice as numerous in the cylinder as outside.

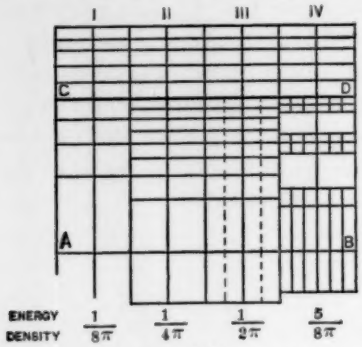


Fig. 1. Half size.

Half of the tubes are supposed to pass through the ether, just as if the iron were not present; the other half go through the iron molecules, which are supposed to fill out the whole volume of the cylinder.

The energy density in the air is $\frac{1}{8\pi}$, in the iron $\frac{1}{4\pi}$. The polarization is $\frac{1}{4\pi}$ in the air, and $\frac{1}{2\pi}$ in the cylinder.

Maxwell does not say anything about the energy density according to Ampère's theory of elementary current magnets. From the nature of the case any exact determination seems impossible, but some idea can be obtained by making certain assumptions with regard to the distribution of the elements, and supposing that the amount of conducting material is very small.

Suppose that the cylinder is saturated, and that all the elements are set at right angles to the field of force. In order to obtain a minimum value for the directed energy density we will assume that the elementary magnets consist of thin wires of infinite conductivity, bent into square or hexagonal circuits, which, for the sake of simplicity, are taken as arranged regularly in long lines side by side so as to form square or hexagonal magnetic solenoids. These latter are to fit together so as to leave only very narrow cracks between them. The permeability of the ether between the conductors and of the conductors themselves is unity.

Then the polarization inside each solenoid due to the currents in the elementary circuits is I, and to this must be added D', the polarization which would exist there if the iron were not present. Thus the total polarization is $D = D' + I$. In the very narrow cracks between the solenoids the polarization is D', the same as that in the space outside, and the distance between the equipotential surfaces is $\frac{1}{4\pi D'}$. The equipotential

surfaces in the cracks are then simply continuations of the plane equipotential surfaces in the air around the iron. The energy density in the crack is $2\pi D'^2$. The distance between the equipotential surfaces inside the solenoids is $\frac{1}{4\pi D}$, and this is to the distance in the outside field in the ratio $D' : D$.

The density of the energy directed parallel with the field inside the solenoid is $2\pi D^2$.

Since the cracks are very narrow, this will be the density of the directed energy in the iron.

With an induction of 20,000 lines per square centimeter, this gives about 16,000,000 ergs per cubic centimeter, or about four-tenths of a calorie.

An attempt is made to represent the equipotential surfaces and polarization tubes according to this hypothesis in Diagram III., Fig. 1. The full vertical lines represent equipotential surfaces, both within and without the iron, while the dotted lines are additional equipotential surfaces inside the solenoids. $\mu = 2$, $B' = 1$, $D' = \frac{1}{4\pi}$, $D = \frac{1}{2\pi}$. Energy density in air $= \frac{1}{8\pi}$, in iron $= \frac{1}{2\pi}$, or twice as great as in Diagram II. Length of polarization cell in air and in cracks = one centimeter, length in solenoids = half a centimeter.

It is certain that the elementary circuits do not fill out the space in this way. If they did, the induction would soon reach a limit, beyond which it could not rise. For each of the elementary circuits is a perfect conductor, and on being turned round so that its axis is parallel to the field, will prevent any additional lines from passing through it, if there is an increase in the field.

The facts of saturation seem to indicate that the space guarded from the entrance of external lines by the elementary magnets is very small.

The molecules of magnetized iron are in all probability distributed very irregularly, but the problem can be simplified by assuming that they form long solenoids when the iron is saturated, and that these solenoids only occupy $\frac{1}{n}$th of the whole volume. The following results can be deduced.

The polarization D'' inside these solenoids remains constant from the moment they are formed, the current in the elementary magnets decreasing as the external field increases.

The average polarization of a cubic centimeter of the iron is

$$D = \frac{1}{n} D'' + \frac{n-1}{n} D'.$$

The quantity known as intensity of magnetization is defined by the equation

$$D = D' + I.$$

Thus

$$I = \frac{D'' - D'}{n},$$

or I diminishes after the constant value of D'' has been reached, the diminution being $\frac{1}{n}$th of the increase of D'. If n is large, this diminution will be small, and I will be fairly constant through a large range if $n = 100$.

The amount of energy in a cubic centimeter will be

$$\frac{2\pi}{n} D''^2 + \frac{2\pi(n-1)}{n} D^2.$$

Taking certain results of Ewing on induction in iron in high magnetic fields and making $n = 100$, the amount of energy in one cubic centimeter is found to be 45 calories. This may perhaps be regarded as a maximum value.

In Diagram IV., Fig. 1, the condition of a portion of a very long cylinder in a uniform field $H = 1$ is indicated, on the assumption that $n = 2$, and μ the ratio between the average polarization of the paramagnetic substance and that in the intermolecular spaces is also two. The polarization outside the cylinder is $\frac{1}{4\pi}$, while the average polarization inside is $\frac{1}{2\pi}$, as in the two former cases.

One half of the space is occupied by the solenoidal molecular chains, which are represented in the figure, suitably divided by the polarization tubes and equipotential surfaces. These are of course much nearer together inside the solenoids than outside.

The polarization inside the solenoids is $\frac{3}{4\pi}$. Each of the cells shown, the volume of which is 4π c.c. outside the solenoids, and $\frac{4\pi}{9}$ c.c. inside, contains half an erg of energy; so that the energy density outside the solenoids is $\frac{1}{8\pi}$. Inside it is $\frac{9}{8\pi}$, and the average energy density in the cylinder is $\frac{5}{8\pi}$, as against $\frac{1}{8\pi}$ in the surrounding field, $\frac{1}{2\pi}$ inside the cylinder of Diagram III., and $\frac{1}{4\pi}$ in Diagram II.

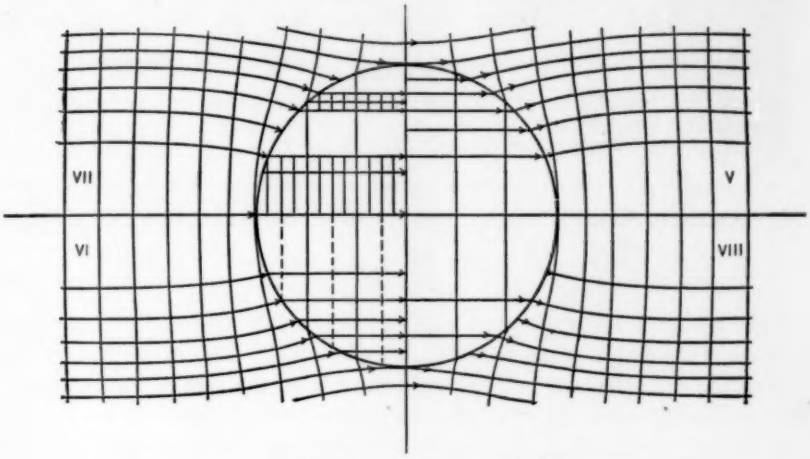
Diagram V., Fig. 2, shows the result, according to the ordinary induction theory, of placing a sphere of radius 4 and permeability 2 in a unit field $B' = 1$. Inside the sphere are shown the equipotential surfaces $V' = -\frac{3B'x}{\mu + 2}$ which are $\frac{4}{3}$ cm. apart. At right angles to these run the

tubes of polarization, which are bounded by the cylindrical surfaces traced out by the horizontal lines, when the figure is revolved about the horizontal diameter of the sphere. Of these there are

$$D = \frac{B}{4\pi} = \frac{3\mu B'}{4\pi(\mu+2)} = \frac{3}{8\pi} \text{ per square centimeter.}$$

Hence through the 16π square centimeters of the equatorial plane there pass six of these polarization tubes, while in the original field, before the sphere was introduced, four tubes passed through the same area.

The polarization tubes outside the sphere are continuous on the surface with those inside, and at a distance from the sphere they become identical



Energy density in V $= \frac{9}{64\pi}$, VI $= \frac{9}{32\pi}$, VII $= \frac{27}{64\pi}$, VIII $= \frac{9}{128\pi}$.

Fig. 2. Half size.

with those due to the field $H' = B' = 1$. The intensity of magnetization is $\frac{3}{16\pi}$, and the polarization of the ether in the sphere is also $\frac{3}{16\pi}$, making a total polarization of $\frac{3}{8\pi}$ in the sphere as compared with $\frac{1}{4\pi}$ in the air at a distance. The energy density is only $\frac{9}{64\pi}$ in the sphere, while it is $\frac{1}{8\pi}$ in the original field.

Diagram VI., Fig. 2, shows the same problem treated so as to represent Ampère's theory, the molecular circuits being supposed to fill out the whole volume, as is also the case in Diagram III., Fig. 1. The dotted lines represent equipotential surfaces inside the solenoids, but not in the narrow cracks between them.

The energy density is twice as great as in the former case, being

$$2\pi D^2 = \frac{9}{32\pi}.$$

In Diagram VII., Fig. 2, the molecular chains or solenoids are only supposed to occupy one-third of the volume of the sphere.

In reality of course these solenoids must be supposed to be very narrow in comparison to their length, and the difficulty observed in the diagram, with regard to the connection between the tubes inside the sphere and those outside, does not occur.

If these solenoids could exist without the presence of the external field, they would send tubes back in the negative direction through the empty spaces between them, so that the polarization in these spaces when the external field is present is only $\frac{3}{16\pi}$, whereas in the distant parts of the external field it is $\frac{1}{4\pi}$. Inside the molecular solenoids the polarization is $\frac{3}{4\pi}$. The total flow of polarization through the sphere is the same in Diagrams V., VI., and VII. The energy density in the sphere is in this last case $\frac{27}{64\pi}$, or 50 per cent greater than in Diagram VI.

Diagram VIII., Fig. 2, shows a sphere of insulating material, the dielectric constant of which is unity. The electrical density on its surface is

$$\sigma = \frac{3}{16\pi} \cdot \cos\theta.$$

The sphere is suspended in a uniform electrostatic field $B'_e = 1$, so that the line $\theta = 0$ points along the direction of the field.

Outside the sphere the electrostatic equipotential surfaces and polarization tubes are geometrically identical with the magnetic lines in the previous cases. Within the sphere the equipotential surfaces are identical with those of Diagram V.

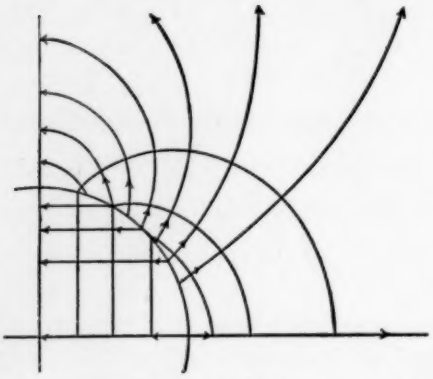


Fig. 3. Half size.

The electrostatic field intensity inside the sphere is only $\frac{3}{4}H'$, and the polarization is $\frac{3}{16\pi}$. The energy density is only $\frac{9}{128\pi}$. Three of the six tubes which come to the surface of the sphere on the negative side end in the three units of negative electricity distributed over that side, while three of the six tubes that start from the positive side, have their origin in the three units of positive electricity on that side. The remaining three tubes from the external field pass through the sphere.

The reason for the fact that the field in the sphere is smaller than that at a distance, is of course that the given electrical distribution would, if acting by itself, produce inside the sphere a field in the negative direction, as indicated in Fig. 3, the field intensity being $-\frac{1}{4}H'$. This is the "demagnetizing effect of the ends" of which we hear when instead of electric charges "free magnetisms" are supposed to exist on the surface of the sphere. It seems as though it would be almost worth while to treat all problems in which this mathematical method is simplest by means of the electrostatic analogy. That is, never to speak of free magnetism, but to work out the electrostatic problem, and to state that the required magnetic field is mathematically the same as the electrostatic field, wherever the permeability is unity.

While there may be nothing very new in what precedes, it is hoped that the diagrams with their explanations may prove of some use to those who, like the author, have experienced difficulty in keeping the different magnetic theories clearly separated.

UNIVERSITY OF NEBRASKA.

ON THE ALTERNATING CURRENT DYNAMO.

By W. E. GOLDSBOROUGH.

CONSIDER the case of a simple alternator having but one armature coil that rotates in a magnetic field of uniform intensity about an axis at right angles to the direction of the lines of force. If successive instants of time during one revolution of the coil are counted from the instant that the coil passes a line drawn through its axis of rotation and perpendicular to both the axis of rotation and the direction of the magnetic flux, the value of the induction piercing the coil at any instant during one cycle is expressed by the equation

$$N = N_{max} \cos \omega t, \tag{1}$$

in which N_{max} equals that portion of the flux that passes through the coil at the instant the plane of the coil is at right angles to the direction of the lines of force, and ω represents its angular velocity. The instantaneous value of the E.M.F. generated in the coil will be, by Faraday's law,

$$e = -\frac{dN}{dt} = \omega N_{max} \sin \omega t = E \sin \omega t, \tag{2}$$

since its maximum value $$E = \omega N_{max}. \tag{3}$$

If the coil is closed through a circuit of resistance R', inductance L' and capacity C', the resistance and inductance of the coil itself being R

and L respectively, a current i will begin to circulate, and we can write the equation of E.M.F.'s of the circuit in the form

$$e=(R+R')i+(L+L')\frac{di}{dt}+\frac{\int idt}{C'}.$$

From this expression we can derive the equation of the current in terms of the constants of the circuit and the maximum value of the E.M.F. developed in the coil and obtain

$$i=\frac{E}{\sqrt{[R+R']^2+\left[\frac{1}{C'\omega}-(L+L')\omega\right]^2}}$$

$$\sin\left\{\omega t-\tan^{-1}\left[\frac{1}{C'_1\omega(R+R')}-\frac{(L+L')\omega}{R+R'}\right]\right\} \qquad (4)$$

which expresses the instantaneous value of i as soon as a condition of cyclic stability has been attained.

Equations (1), (2), and (4) are the general equations that cover the working of alternating current dynamos; they have been subjected to graphical analysis, the results of which are exhibited in Fig. 1, and are discussed in the following paragraphs:

Suppose a circuit in which the inductance is zero, the capacity infinite, and the resistance variable, to be subjected to the influence of a simple harmonic E.M.F. that is generated by an alternator having a constant armature inductance for all values of armature current, a constant field excitation and a constant speed. Under these conditions, the virtual value of the E.M.F. at the brushes of the alternator just before the circuit is closed will be

$$\bar{E}=\omega N_{\max}\div\sqrt{2}, \qquad (5)$$

which is represented by the vector OA in the figure. The vector ON is laid off at right angles to OA to represent the value of the M.M.F. producing $N_{\max}$. It is drawn 90° in advance of the E.M.F. it induces in accordance with the relation exhibited in equations (1) and (2). At the time of closing the circuit, suppose the external variable non-inductive resistance to have a value R', and that the constant armature resistance has a value R, and the constant armature inductance a value L. Then the equation of the current will assume the form

$$i=\frac{E}{(\sqrt{R+R'})^2+L^2\omega^2}\sin\left[\omega t-\tan^{-1}\frac{L\omega}{R+R'}\right] \qquad (6)$$

and its virtual value $$\bar{I}=\frac{\bar{E}}{\sqrt{(R+R')^2+L^2\omega^2}}, \qquad (7)$$

which we can represent[1] by the vector OB_0 lagging $\tan^{-1}\frac{L\omega}{R+R'}$ degrees behind OA. This armature current will react upon the magnetizing forces

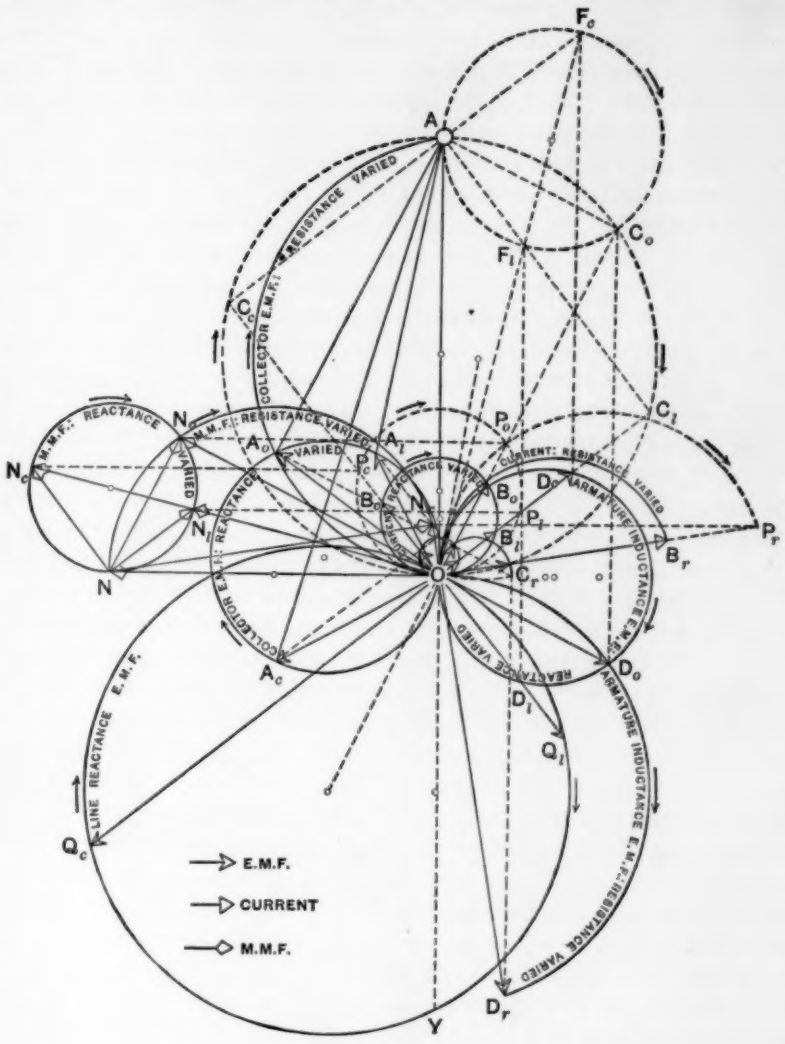


Fig. 1.

[1] The subscript letter (*o*) refers to the initial condition.
The subscript letter (*r*) refers to changes in the line *resistance*.
The subscript letter (*l*) refers to changes in the line *inductance*.
The subscript letter (*c*) refers to changes in the *capacity* of the line.

due to the constant field excitation, and by virtue of the inductance of the armature will produce an M.M.F. in phase with itself which is represented by the vector NN_0, drawn parallel to the current vector from the positive extremity of ON. This armature M.M.F. sets up a cyclic magnetization developing a counter E.M.F. OD_0 lagging 90° behind the current, and there is a loss of effective E.M.F. due to the armature resistance that is shown by the short E.M.F. vector in phase with OB_0; therefore the total loss of E.M.F. in the armature will be the resultant of these two vectors or OA_0. The effective E.M.F. that overcomes the resistance of the non-inductive external circuit will be the vector A_0A, since it completes the E.M.F. triangle on OA and is in phase with the current OB_0. The total effective E.M.F. (OC_0) that overcomes the total ohmic resistance $(R+R')$ of the circuit, is due to the cyclic magnetization set up by the M.M.F. vector ON_0. ON_0 is the resultant of ON and NN_0, and as shown by the geometry of the figure, it is 90° in advance of the current, and therefore of A_0A, as it should be. The projection of NN_0 on ON is the component of the armature M.M.F. that acts against the field magnetization, *i.e.* it is *a measure of the armature reaction*. The projection of NN_0 on OA is likewise a measure of the cross-magnetizing action of the armature.

Having constructed the initial diagram, we can now follow out what takes place when the resistance of the external circuit is varied. Suppose R' is reduced to a value R_r. The current vector head B_0 will move out along the semicircle OB_0B_r until equilibrium is again established in the circuit by the current reaching its maximum possible value under the new conditions.[1] The vectors OA and ON retaining their positions, all the other vectors involved will reach their final values corresponding to the new current by following the arcs of the circles passing through their positive extremities to the positions designated by the common subscript letter (r). The correctness of the variations indicated can be readily verified by an inspection of the geometry of the figure in connection with equation (7).

In the present case, R' has been reduced to zero; in other words, the subscripts (r) indicate what takes place when a machine whose armature inductance is large, as well as constant, is short-circuited. A_0 moves up to A, and the E.M.F. at the brushes is zero. The current assumes an angle of lag of almost 90° behind the total internal armature E.M.F. OA, the *armature reaction* almost counterbalances the M.M.F. of the fields, and the resultant M.M.F. ON_r is just sufficient to develop the E.M.F. OC_r that overcomes the resistance of the armature.

Returning to the initial conditions, suppose we increase the value of L' from zero to some value L_1, *i.e.* suppose we introduce inductance into

[1] See Bedell and Crehore's Alternating Currents, p. 223.

the external circuit. The virtual value of the current will then be expressed by the equation

$$\bar{I} = \frac{\bar{E}}{\sqrt{(R+R')^2 + (L+L_1)^2\omega^2}}, \tag{8}$$

and it will lag behind the internal E.M.F. $\bar{E}$ or OA by an angle

$$\phi = \tan^{-1}\left(\frac{L+L_1}{R+R'}\omega\right). \tag{9}$$

Referring to the figure, the new positions assumed by the variable vectors, owing to the introduction of L_1, are designated by the subscript letter (1). The current will decrease and its vector head move along the circle $OB_cB_0B_1O$ until a state of equilibrium exists between the forces involved. The E.M.F. that overcomes the resistance and inductance of the armature will decrease also and move to the position OA_1, its vector head following the circle $OA_cA_0A_1O$, and the E.M.F. at the collector rings will first decrease and then increase to a final value A_1A. The introduction of inductance into the external circuit brings the E.M.F. at the collector rings and the total internal E.M.F. (OA) more nearly into phase; it however causes a lag angle F_1OB_1 to be introduced between the collector E.M.F. and the current. The inductance E.M.F. of the armature decreases along the circle $OD_cD_0D_1O$ to a value OD_1, and the inductance E.M.F. of the external circuit increases from zero along the circle YQ_cOQ_1Y to a value OQ_1. The resultant M.M.F. will be ON_1, and it is seen that while the armature reaction has remained very nearly constant, the cross-magnetizing effect has been reduced about fifty per cent.

From our initial conditions as indicated by the subscript letter (o), we can also study the effects produced by the introduction of capacity into the external circuit. If the value of C' is reduced from infinity to some value C_c, the virtual value of the current will change to

$$\bar{I} = \frac{\bar{E}}{\sqrt{(R+R')^2 + \left(\frac{1}{C_c\omega} - L\omega\right)^2}}, \tag{10}$$

and the angle between OA and the current will have a value

$$\phi = \tan^{-1}\left[\frac{1}{(R+R')C_c\omega} - \frac{L\omega}{(R+R')}\right]. \tag{11}$$

In consequence of this change the current vector will assume the position OB_c, and the other variable vectors will move to their corresponding positions shown by the subscript letter (c). The current in its new position is not only in advance of the E.M.F. (A_cO) at the brushes, but is also in

advance of the E.M.F. OA, since it has moved from B_0 to a maximum value when passing OA, and then decreased in value.[1]

The collector E.M.F., on the other hand, steadily increases as the capacity decreases, till it reaches a value A_cA much greater than the open circuit E.M.F. of the machine. A resonant effect comes into play here after the capacity of the line neutralizes the inductance of the armature that is very well illustrated by the figure; the line A_cA will be a maximum when it passes from A through the center of the circle $OA_cA_0A_1O$, and will represent the greatest difference of potential that can possibly exist between the brushes so long as R and R' remain unchanged in value. This rise in potential is due to the current being in *advance of the vector* OA, for the position of the armature M.M.F. vector is also advanced, and NN_c increases the total flux in the air gap instead of diminishing it. The cross-magnetizing action of the armature, however, remains approximately the same.

The introduction of capacity into the line causes the inductance E.M.F. of the armature to move to the position D_c, and the reactance E.M.F. of the external circuit to decrease through zero and then increasing, assume a position Q_cO, considerably in advance of the collector E.M.F., and 90° in advance of the current OB_c.

The arrows indicate the relative direction of motion of the vectors as the resistance is varied from infinity to zero, or as the reactance is carried from zero capacity to an infinite inductance.

By following out a similar line of constructions the effects produced by variations of the armature inductance can be studied, and by successively varying the resistance, inductance, capacity, and frequency constants, and constructing corresponding diagrams, a large variety of problems involving the simultaneous variation of several terms can be successfully treated.

[1] See Bedell and Crehore's Alternating Currents, p. 297.

NEW BOOKS.

A New View of the Origin of Dalton's Atomic Theory: A Contribution to Chemical History, together with Letters and Documents concerning the Life and Labours of John Dalton, now for the first time published from Manuscript in the Possession of the Literary and Philosophical Society of Manchester. By HENRY E. ROSCOE and ARTHUR HARDEN. 8vo, pp. x+191. London and New York, Macmillan & Co., 1896.

The happy discovery, in the rooms of the Literary and Philosophical Society of Manchester, of a number of manuscript volumes in the handwriting of John Dalton, has thrown a new light upon the genesis of his ideas. The precious documents comprise an extensive series of laboratory notes, beginning with the year 1802, and continuing to Dalton's latest years, bound in twelve volumes, as well as lecture notes of six lectures delivered in 1810 by Dalton at the Royal Institution, London. The laboratory note-books contain an almost unbroken record of the experimental work conducted in the rooms of the Manchester Society, and which supplied him with the materials embodied in his great work, *A New System of Chemical Philosophy*.

It has hitherto been supposed that it was the experimental discovery of the law of combination in multiple proportions that led Dalton to conceive of the chemical combination of atoms having definite weights, the atomic theory being thus adopted to explain the facts ascertained by chemical analysis. But an examination of the newly found papers shows that Dalton approached the atomic theory from a physical standpoint, he being an adherent of the Newtonian doctrine of the atomic constitution of matter.

The first part of the volume contains details of the evidence on which the above conclusion is founded; this is followed by a short epitome of Dalton's daily laboratory notes from 1802 to 1808, and by a discussion of the successive series of numbers given by Dalton as representing the atomic weights of the elements. The following table of atomic weights was written out Sept. 6, 1803, and is probably the earliest constructed:

Ult. at hydrogen	1.00	Ult. at nitrous oxide	13.66
" oxygen	5.66	" nitric acid	15.32
" azot	4.00	" sulphur	17.00
" carbon (charcoal)	4.50	" sulphurous acid	22.66
" water	6.66	" sulphuric acid	28.32
" ammonia	5.00	" carbonic acid	15.80
" nitrous gas	9.66	" oxide of carbone	10.20

Chapter V. contains letters written and received by Dalton; among the latter are a few from Berzelius, Thomas Thomson, and Davy. The book is well printed, and the facsimiles of Dalton's MS. add to the interest of a valuable contribution to the history of chemistry. There is no index.

H. CARRINGTON BOLTON.

A Laboratory Course in Experimental Physics. By W. J. LOUDON and J. C. MCLENNAN. 8vo, pp. 302. Macmillan & Co., 1895.

A little more than a quarter of a century ago, the first laboratory guide-book in physics was published in Leipzig. The author was Friedrich Kohlrausch, and his *Leitfaden* is still a standard for most of the teachers of physics who have studied in Germany. But the book is so solid, so compact, that the elementary student who has no supplementary instructions is sure to be discouraged by its use, whether he employs the German edition or the English translation. It was natural, therefore, after laboratory methods had become generally introduced, that new guide-books should come forth to compete for popular favor, such as the well-known manuals by Pickering, Stewart, and Gee, and Glazebrook and Shaw. At present, we may safely look for one or more new ones each year.

Every such guide-book is the outcome of the author's own experience and necessities, and is published in the belief that its sphere of usefulness may extend beyond the laboratory for which it was primarily intended. It would be interesting to examine statistical returns, if such were available, with a view to ascertaining to what extent any such book is systematically employed in any laboratory with which the author has no immediate connection. The case is quite different from that of a class text-book, in which lessons are assigned for which the student is held responsible, or which is assumed as the accompaniment of a systematic course of lectures. In every college, a course of practical laboratory exercises in physics is given as the needful preparation for subsequent work of investigation; and a majority of the students never advance beyond this prescribed course in manipulation. Most generally this work is done under the supervision of an instructor who has but little leisure, and each exercise is undertaken by the students in rotation. The immediate object of a laboratory manual is, therefore, to economize the students' time and the instructor's labor. Instead of giving the same oral instruction, in succession, to scores of students, it is best to write out what the student needs, and let this specific instruction, on paper or cardboard, be found with the apparatus to which it refers. The expenditure of breath and of patience is thus reduced to a minimum. Such instruction-cards can be so prepared as to leave room for

the exercise of ingenuity and thought on the part of the student; but such directions as they convey must be explicit, and adapted to the exact apparatus which the student is about to handle.

No two laboratories are alike in equipment. Whatever is written for one will be found, for any other, to be lacking in many indispensable details, and overburdened with much unavailable material. A variety of laboratory manuals must be at hand for reference-books, but not one of them can alone be a satisfactory guide. Most of them will receive but scant attention from the ordinary student if his instruction-cards have been well prepared. He will frequently consult tables of constants, and, in studying out the construction of an unfamiliar instrument, printed descriptions are often valuable. But such a description is quite as apt to be found in a dealer's catalogue, or a comprehensive text-book, as in any one of an assortment of laboratory guide-books.

Every laboratory instructor, therefore, finds it necessary to write his own guide-book, either in part or in whole. In doing so, he will naturally consult other guide-books, but adopt none. The volume by Loudon and McLennan is, doubtless, well suited for the students in the Toronto laboratory, where the collection of expensive and historical apparatus is evidently uncommonly fine. Part I. is devoted to an elementary course in which very excellent instructions are given for the standard beginner's exercises, such as measurements of length, volume, and density; but no discussion or guidance is offered regarding the measurement of mass. Quite probably, the students for whom the book was prepared receive training in the chemical laboratory, and thus acquire some familiarity with the use of the physical balance before beginning physical laboratory work. If so, this removes the necessity for teaching anything about the sensibility of the balance, and the precautions required for accurate weighing; but, for other laboratories, such an omission in a guide-book is serious. Exercises are provided for the testing of Boyle's law, the determination of capillary constants, specific heat, and heat of fusion, and quite a number in relation to mirrors, lenses, and photometry.

Part II. is a more advanced course devoted to work in acoustics, heat, magnetism, and electricity, followed by an appendix on the determination of gravity, and on the torsion-pendulum. The portion devoted to acoustics is exceptionally large, more than half as much as that assigned to electricity. It includes theoretical discussion and quantitative work in relation to pitch and musical quality, harmonic motion, optical methods of tuning, and several methods of measuring the velocity of sound. The Toronto laboratory is evidently well provided with König's best apparatus, including such pieces as the expensive Helmholtz outfit for synthesis, and Regnault's contrivance for studying the velocity of sound in gases. What is more remark-

able is that this apparatus is actually used, instead of being kept merely on display for historical purposes. Of late years, acoustics has been so generally relegated to the background, to make room for electricity, that the exhibition of serious interest in it, in an American college, is a refreshing evidence of scientific courage and unselfish zeal.

The list of advanced experiments in heat covers considerable ground, and implies the possession of such instruments as Favre and Silbermann's calorimeter, and Regnault's apparatus for hygrometry, specific heat of gases, and energy of change of state. These may be legitimately regarded as laboratory luxuries. Access to them is impossible for perhaps a majority of those who read the book. Important as was the work of these distinguished physicists, it may be questionable whether the exact duplication of such historic apparatus is now really to be desired in a student-laboratory. If the student undertakes similar research, the outlay would, perhaps, better be spent in the construction of appliances due to his own adaptation of means to ends. In the repetition of what is historic, there should be wide room for variation.

The section assigned to electricity and magnetism is made unnecessarily diffuse by the introduction of much material that is better introduced in a lecture course of general instruction. It is fair to assume that elementary definitions, such as that "two magnetic poles of the same kind repel," are unnecessary for the student who is at all fit to enter the physical laboratory. There is, possibly, room for difference of opinion about the extent to which qualitative observation may be accepted in lieu of quantitative measurement in the student-laboratory, but there are few, to-day, who think that even the simplest laws of nature should be rediscovered by elementary students. The last thirty pages of the section contain an excellent exposition of methods in the electrical laboratory; but, of the preceding sixty pages, the greater part belongs more properly to the general text-book than to the laboratory guide.

Throughout the book, it may be said that the discussion of general principles has occupied space that would better have been devoted to precautions for securing accuracy, and to the consideration of numerical examples. As an aid to those who prepare their own laboratory instruction-cards, this volume will be found very useful, and it is a welcome addition to the laboratory book-shelf; but, as a practical guide to the ordinary student, in an ordinary laboratory, its usefulness will be less wide than one may naturally wish on account of its general attractiveness.

W. LECONTE STEVENS.

A Primer of the History of Mathematics. By W. W. Rouse Ball. 8vo, pp. 146. Macmillan & Co., 1895.

Of all sorts and conditions of books that fall to the lot of the reviewer, one of this kind is the most difficult to fairly judge. One cannot say that it is unscientific, for it makes no pretensions to be otherwise; neither can one say that it is wanting in seriousness, for it will at once assert that seriousness is the farthest from its thoughts. If you assert that it gives no adequate view of mathematics of this century, it replies that that is not its humble mission, and, if you say that it wastes its pages in story-telling, it at once retorts that it caters to readers who must be brought to better things by just that diet. And the critic who sets his "five wits on the stretch" to demolish the work at the stroke of the pen finds himself helplessly repeating, "Is one mocked by an elf?" before he has fairly begun.

The fact is, for what the work pretends to be, it is well written, and may be called a decided success. A *multum in parvo*, it supplies, at a trifling expense, a handbook that will serve the purposes of elementary students and teachers who cannot afford the more elaborate and expensive treatises.

The first thing liable to impress the reader unfavorably is the apportionment of matter. Forty per cent of the pages have to do with mathematics before the Renaissance, and one-seventh of the work is devoted to the mediæval period, both being entirely disproportionate allowances. But when it is considered that this is a handbook for students who are reading the mere elements of the subject, and that these elements were largely developed before the Renaissance, the fault seems less prominent.

Nevertheless, it cannot be denied that here is the real weakness of the book, and the more one considers it the more serious it becomes. One feels that a line apiece to familiar names like Monge, Carnot, and Poncelet, and not a syllable for Möbius, fits hardly with a page on Roger Bacon, and a considerable setting forth of tradition about Thales, Pythagoras, Archimedes, and other worthies. And when one reads the further gossip, interesting but not very valuable, about Kepler's trouble with his first wife, and his method of courting his second, and about Tartaglia, Lagrange, Laplace, and others, he wonders if, after all, the elementary reader might not be better served by the mention of a few of the many familiar names which are omitted. As examples of names, almost every one of which finds place in text-books of quite an elementary grade, and for which readers of the *Primer* will seek information in vain, the following may be mentioned: Argand, Galois, Horner, Wilson, Plücker, Gudermann, Bezout, Vandermonde, Sarrus, Cramer, Landen, Malfatti, Matthew Stewart, Arbogaste, Mascheroni, L'Huilier, Maupertuis, Gergonne, Quetelet, Bellavitis, Clifford, with many others.

Furthermore, out of all proportion to the importance of their contributions are the apportionments between certain individuals. Jordanus gets fifteen times as much space as De Moivre, Roger Bacon eighteen times as much as Roger Cotes, and Regiomontanus twenty times as much as Poncelet. While Pacioli gets two pages, Von Staudt gets a quarter of a page; while Pascal gets three pages and a half, and certainly deserves generous treatment, Cayley, Riemann, and Steiner get along with half a page each.

The mathematics of the present century can hardly expect any generous treatment in a work of this nature. But such common names as those of Brianchon and Feuerbach in elementary geometry, or Lobachevsky and Bolyai in the non-Euclidean, or those of the creators of the recent geometry of the triangle, — Lemoine, Brocard, Tucker, and others; or Klein, Fuchs, Hermite, and Sylvester, — since living writers are not wholly excluded; or Clebsch and Hesse, — one cannot reconcile the omission of typical names like these, representing movements more or less familiar to all, with the presence of names of lesser note.

Of course, the work has its share of misprints, which is merely another way of saying that it is still in its first edition. Among them are: *iscosahedron* (p. 7); *octrahedron* (p. 7); δύναμίς (p. 32); 1621, for 1620, as the date of Harriot's death (p. 68); 1576, for March 5, 1574–5, as the date of Oughtred's birth (p. 68); improper spacing between the E's and F's in the index, etc. These dates are all right in the second edition of the author's larger history, and so are manifestly misprints here.

There are also some chronological errors which cannot be so easily explained away. That Abel's theorem was "written in 1828" is true, but it was not first written in that year. It was in Abel's possession as early as 1825, the year in which he first went to Paris, and it was made public in 1826. In cases of uncertainty of date, the author usually and commendably resorts to the word "about" or "*circa*"; but, in the case of Girard, he says "1590–1633," though each date is quite uncertain; similarly, for several other dates, including that of Lord Brouncker's birth, which, unless Mr. Ball has found some new documentary evidence, is also quite doubtful. Documentary evidence suggests the case of the date of Briggs's birth. The author and, rather strangely, Cantor, who is usually very exact in details, give 1556. The older writers all give that date, some with a *circa*. Since Whittaker's sketch in the *Dictionary of National Biography*, in which it is stated that Briggs was born "in February, 1560–1, according to the entry in the Halifax parish register," the recent encyclopedias have adopted this date. It would be interesting to know if there is longer any doubt about the matter. A rather strange error which has run through each edition of the larger work, and which now appears in the *Primer*, is the statement that "the only regular polygons which can be constructed by

elementary geometry are those of which the number of sides is $2^m(2^n + 1)$, where m and n are integers, and $2^n + 1$ is a prime." This excludes the pentedecagon, and, unless zero be reckoned an integer, the triangle, pentagon, and others.

It must be confessed, however, that the essential features of criticism are, largely, matters of judgment which depend upon the point of view. It is doubtful if any one else would have succeeded better in the selection of matter, or would have presented the subject in as happy a style as that which characterizes all of Mr. Ball's contributions to the history of mathematics.

DAVID EUGENE SMITH.

MICHIGAN STATE NORMAL SCHOOL, YPSILANTI.

Étude Analytique et Graphique des Courants Alternatifs. Par F. BEDELL et A. C. CREHORE. Traduit par J. BERTHON, Ingénieur des Arts et Manufactures. 8vo, pp. 261. Éditeur, Georges Carré, 3 Rue Racine, Paris, 1895.

Theorie der Wechselströme in analytischer und graphischer Darstellung. Von Dr. FREDERICK BEDELL and Dr. A. C. CREHORE. Uebersetzt von ALFRED H. BUCHERER. 8vo, pp. 266. Berlin, Julius Springer, and München, R. Oldenbourg, 1895.

Perhaps the best proof that the theoretical work of American scientists is gaining recognition abroad is the fact that American treatises are now being translated into the Continental languages. That a mathematical work, even though pertaining to practical applications, should be deemed worthy of translation into the French and German languages, already rich in works of this nature, and particularly upon the alternating current, must be gratifying to the authors; for though perhaps not the birthplace of the alternating current, the Continent may justly be looked upon as the fatherland of the commercial applications. Both translations follow the original very closely, the intention evidently being to give the original authors full credit for their work. On many points there may arise a divergence of opinion, as, for instance, when the translators choose for the word *medium* the German *mittel* and the French *milieu*, while medium in German and medium in French express the English meaning of medium exactly. Professor Foeppl, a German authority on electro-mathematics, uses the word *medium* in his theoretical demonstrations, while, on the other hand, Mr. Vashy, the well-known French theorist, uses *milieu*. Mr. Bucherer adopts the English style of denoting the arc of tangent by $\tan^{-1}$, instead of the more common German arc-tang, while Mr. Berthon seems to prefer the

latter denomination. Drs. Bedell and Crehore followed Mr. Steinmetz's example in denoting $\sqrt{-1}$ by j instead of i, which is of importance in a treatise like the one under consideration, where the instantaneous value of the current, usually denoted by i, occurs so frequently. Mr. Bucherer seemed to be more radical in his views, and accepted the given hint, while Mr. Berthon avoids committing himself by clinging throughout to $\sqrt{-1}$. When it comes to the solution of the linear differential equations for the current, Mr. Bucherer follows the authors verbally, naturally omitting the references to Johnson's *Differential Equations* Mr. Berthon hesitated to follow this practice, which seems creditable, as Johnson's book is not known to any extent in France and Germany; he pronounces the American authors' method somewhat "peculiar," and applies a method commonly taught in Continental treatises of analysis, avoiding even a repetition of the solution by using a different one on each occasion. In the second part of the book, the graphical treatment, the originality of the American authors is strictly preserved. The careful work of the translators, and the original merit of the treatise, should ensure a hearty reception to the work which naturally must add to the appreciation and regard for American works in general.

F. J. DOMMERQUE.

Computation Rules and Logarithms, with Tables of Other Useful Functions. By S. W. HOLMAN. pp. xlv + 73. Macmillan & Co., 1896.

In the selection and arrangement of the material for this book, the author has shown exceeding care. The attention given by him to correctness in mechanical detail, adds not only to the pleasing effect produced by the book, but also to its efficiency and the facility with which it may be used. The logarithms (4 and 5 place) and other tables have been arranged with reference to rapidity in their use with minimum mental effort, type and spacing being selected with this end in view.

The first portion of this book gives directions for the rejection or retention of significant figures and other computation rules and directions for the use of the tables. B.

A Text-book of Gas Manufacture. For students. By JOHN HORNBY. pp. xii + 261. London, George Bell & Sons, 1896. (*Received.*)

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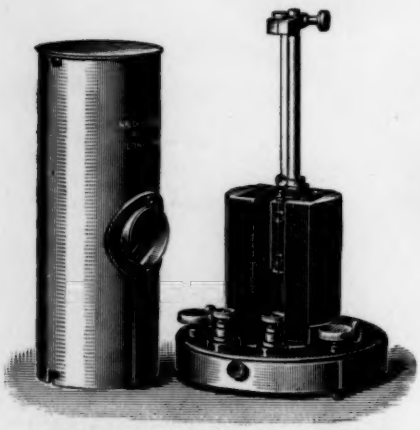

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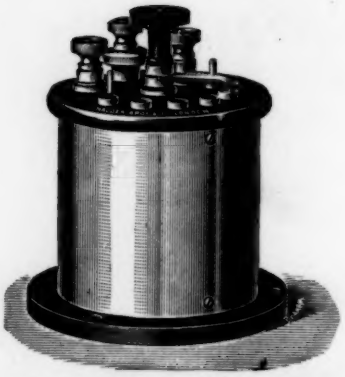

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